COMPARISON OF SELECTED EXTRACTANTS FOR POTASSIUM REQUIREMENT FACTOR AND EVALUATING POTASSIUM EQUILIBRIA FOR SOIL TESTING AND FERTILIZER RECOMMENDATIONS

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DECLARATION

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ABSTRACT

Potassium (K) distribution differs among soils because of variation in soil minerals, and the response to K fertilizer applied differs significantly due to this variation. Soil K occurs in soluble, exchangeable, non-exchangeable and structural K forms and soil testing usually analyses exchangeable K for use in fertilizer recommendation in-order to rectify K deficiencies problems. For the appropriate management of K fertilization and K recommendations, potassium equilibria (Q/I potassium relations, Schofield ratio law and soil surface charge characteristics) contribute effectively to estimating K availability and in evaluating potassium's ability in soil solution. The general aim of the study was to study potassium requirement factors and its relation to surface charge characteristics and K equilibria for making fertilizer recommendations. The specific objectives were to (a) Compare KRF derived from various extractants, (b) evaluate Q/I relations and its empirical relation with KRF, (c) establish the conformation to ratio law and (d) evaluate surface charge characteristics on soils and its relation to K equilibria.

Soil samples were collected from the 0-20 cm depth of various regions of KwaZulu-Natal, and analysed for physicochemical properties (clay content, total carbon, exchangeable acidity, total cations, exchangeable K, soil pH and sample density). Textural classes ranged from mostly sandy clay loam to clay with clay content ranging from 6 to 30%. Soil pH (KCl) ranged from acidic (3.78) to near neutral (6.47) for all the studied soils. Mean total carbon value was highest 5.88% for Nitisols, and lowest for Leptosols at 2.11%. Acrisols showed the highest mean exchangeable acidity values (1.12 cmol L^{-1}), and Vertisols having the lowest at 0.15 cmol L^{-1}. The overall mean point of zero salt effect (PZSE) of the soils was 5.39 and it ranged from 4.1 to 7.4, and point of zero net charge (PZNC) of all the soils ranged from 1.2 to 5.2.

The potassium requirement factor (KRF) was evaluated by amending each sample with 0, 30, 90 and 120 mg K kg^{-1} of finely ground potassium dihydrogen phosphate (KH_2PO_4) and incubated for six weeks. The values of KRF expressed as kg K ha^{-1} per mg K L^{-1} ranged from 0.81-1.98; 1.08-3.85 and 0.48-0.90 for Mehlich-3, Ammonium acetate and Bray No.2, respectively. There was a strong correlation observed between Mehlich-3, Ammonium acetate and Bray No.2 extraction (r = 0.81 to 0.85), with the KRF values being poorly correlated with clay % with r = 0.05, 0.07 and 0.13, respectively. Total cations (r = 0.21 to 0.36), carbon (r = 0.10 to 0.33) and pH (KCl) (r = 0.09 to 0.35) showed poor positive correlation with all the evaluated extractants. The study also involved laboratory experiments on Q/I parameters of ten (10) soils selected from various soil groups. The values of equilibrium activity ratio of

potassium (AR^K) ranged between 0.00070 and 0.00275 (mol L^{-1})$^{0.5}$. Labile K values (-ΔK) varied from 0.234 to 0.0471 (cmol/kg). Potassium buffering capacity (PBC^K) of the soils ranged from 62.69 to 95.05 cmol/kg/ (mol L^{-1})$^{0.5}$. The studied extractants correlation coefficient between the K extracted by these two methods ranged at 0.81, indicating a good significant similar extraction behaviour of the two method. The study concluded that, the best suited test method when compared amongst the evaluated extractants Mehlich-3, Ammonium acetate and Bray No.2, would best be the Ammonium acetate and Mehlich-3, which extracted almost similar amounts of soil potassium irrespective of type and initial K status of the soil. In the study Q/I parameters were also investigated for insightful background in how they affect K availability and to making fertilizer recommendations. Therefore in-terms of fertilizer recommendation these Q/I parameters resulted to medium K fertilizer to change the soil unit with an indication of better K availability. The study managed to complement confirmation to ratio law with regards to K availability inorder to make fertilizer K recommendations.

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CHAPTER ONE: GENERAL INTRODUCTION

Soil potassium (K) reserves are crucial for crop yield and quality more so in low input agricultural systems (Andrist Rangel, 2008). Soils contain widely variable pools of K that can be potentially mobilized during chemical weathering of minerals (Simonsson et al., 2009). Available forms of potassium include soluble and exchangeable K, while the non-exchangeable and structural forms in soil are unavailable (Ldigbor et al., 2009). The exchangeable K^+ pool is bound electrostatically as outer-sphere complexation on soil minerals or organic matter and exchanged with other cations such as magnesium (Mg^{2+}) and calcium (Ca^{2+}) and such exchange is considered to be at equilibrium commonly expressed by Schofield Ratio Law (SRL) pK-1/2(pCa + pMg) where p represent natural log or $(K)/(Ca+Mg)^{1/2}$ (Jalali, 2007). On the other-hand, the non-exchangeable K occurs in the interlayer's spaces of minerals.

The addition of fertilizer K in the soil increases soluble K, with a fraction, as per the equilibrium value, of it being adsorbed onto exchange sites while another fraction is fixed into non-exchangeable forms. However, effective distribution of added K amongst the K forms, particularly fixed K, plays a significant role in the soil-plant system influencing effectiveness of fertilization (Goli-Kalanpa et al., 2008). The activity of competing ions (Ca^{2+} and Mg^{2+}) in the soil exchange system also plays a vital role in determining potassium potential. The fertilizer recommendation services, in South Africa has fully adapted to using soil testing, to assist in quantifying and predicting nutrient status likely to impact on crop growth.

Potassium predictions are done through (i) determining the content of labile soil K level based on specific extractants, (ii) further assessing soil K deficit from the known optimum level applicable to the crop in terms of the soil K test. The deficit is converted into a mass of nutrient required per unit area (e.g. kg /K ha^{-1}) by multiplying with a factor reflecting soil properties , which is termed the potassium requirement factor (KRF) (Johnston et al., 1999; Henry and Smith, 2004). The KRF is defined as a soil specific factor which represents the amount of K required per ha for one (1) unit increase in soil test K level and accounts for the effect of K fixation on the recovery of added K (Johnston et al., 1999). The value of KRF varies with other soil characteristics.

Previous studies on KRF, AMBIC has been widely used as an extractants .A study conducted by Johnston et al. (1999) on a wide range of soils from KwaZulu-Natal (South Africa), using AMBIC (NH_4HCO_3/NH_4F/EDTA) solution as an extractant, established that the KRF varied between 1.5 and 8.8 kg K/ha/per unit soil test. Furthermore, Elephant and Miles (2016)

conducted a similar study with a wide range of soils of the South African sugar industry, also using AMBIC solution, and showed that the KRF values varied from 1.56-7.73 kg K/ha/per unit soil test. However, the studies showed poor correlation between KRF and routinely measured soil parameters possibly due, largely, to the fact that KRF is considered to be strongly related to clay mineralogy. The ammonium ion (NH_4^+) is the essential component of the AMBIC and ammonium acetate extractants, which is essential for the extraction of potassium (K^+) from soils because of similar ionic radius and similar behaviour, and as such are the most common extractant used in KZN region (Black, 1968)..

The standard extractant Bray No.2, which is used for effectively extracting plant available phosphorus (P) has also been used for determination of KRF by other studies (Thompson, 1995). The use of Bray No.2 extraction has long been associated with controversy; the study intended to get clarity on its effectiveness in determining labile K. However, there is still uncertainty about the suitability of the Mehlic-3 on soils that are neutral to alkaline and contain free calcium carbonate ($CaCO_3$) (Schmisek et al., 1998). The use of each extractant is usually associated with drawbacks and commonly suitable for specific soil types for example Bray No.2 method makes use of a diluted strong acids plus complexing ions and it a standard routine method for determining phosphorus, while Mehlich-3 and ammonium acetate extractant have been used across a whole range of soil pH values. Therefore, this study aims to evaluate and compare three widely used extractants (Ammonium acetate, Mehlich-3 and Bray No.2) for KRF and further determine for KRF, and also to further determining correlation coefficients between the K extracted by each studied extractant.

Potassium equilibria, and consequently behaviour, is attributed to the K-(Ca+Mg) ternary system of exchange. An approach developed to quantify, characterize and evaluate the soil K availability, mostly based on the method earlier introduced by Beckett, (1964a), has been used to assess K status of soils, through the adoption of the potassium quantity- intensity (Q/I) relation characteristic. The Q/I relationships are based on Schofield ratio law, governed by activity ratio, which is a measure of the availability or intensity (I) of labile K in the soil. However, (Taylor, 1958), when evaluating ion pair K-(Ca+Mg), reported that two out of four soils did not conform to the law while those that strictly obeyed the law were soils only of low K status. The non-conformity of the law is usually affected by the fact that the concentration of soil solution being high enough for anions to penetrate to the inner part of the double layer. If for a given system soils do not obey SRL it would render the use of exchange equations such

as X-Ca + Mg = X-Mg + Ca, and subsequent use of Vanselow, Gapon and similar equations obsolete given that the exchange is not at equilibrium. This will further warrant a revision as to how labile K is presented. However, the law is obeyed under conditions such that all solutions of complement of labile K and Ca in equilibrium would possess the same activity ratio $a_K/\sqrt{(a_{Ca})}$, $a_K/\sqrt{(a_{Mg})}$ (Schofield, 1947a ; Schofield, 1952). South African soils vary in their potassium status from low, through medium to high levels and this may result in large portion of soils not conforming to Schofield ratio law. However, studies that relate conformation to ratio are limited, particularly in South Africa, where they could contribute in relations to understanding K dynamics better. Therefore, the study evaluates whether there could be links between the conformation to ratio law and KRF and fertilizer recommendations.

The ratio law also depends on the charge characteristics of the soil components. Soil charge characteristics have significant implications on the ion exchange, adsorption, and other chemical processes occurring at the liquid/colloid interface. Such reactions control various physicochemical properties of ions (Karak et al., 2005). The surface variable charge depends mostly on activities of potential determining ions (H^+ and OH^-) and electrolyte concentrations as represented by ionic strength. Depending on pH, the surfaces can bear net negative, positive or no charge. Studies to fully articulate the effectiveness of surface charges on soil potassium and their effects on K fertilizer recommendations are required.

The general aim of the study was to study potassium requirement factors and its relation to surface charge characteristics and K equilibria for making fertilizer recommendations. The specific objectives were to (a) Compare KRF derived from various extractants, (b) evaluate Q/I relations and its empirical relation with KRF, (c) establish the conformation to ratio law and (d) evaluate surface charge characteristics on soils and its relation to K equilibria.

CHAPTER TWO: LITERATURE REVIEW

2.1. Introduction

Potassium distribution in the soil environment differs from soil type because of differences in dominant soil minerals, affecting response to K fertilizer applied. The availability and supply of K to crops is affected by various soil K fractions. Exchangeable K and water-soluble K are readily available for plant uptake, while non-exchangeable K, which constitutes a major percentage of total soil K, slowly becomes available through mineral weathering (Sharpley, 1990). The addition of fertilizer K in soil systems results in some portions of it being fixed by soil minerals, which affects availability. However, the fixation of K added in soils is closely related to the parent material, degree of weathering, K gains through fertilizer, surface charge density, and degree of interlaying of clay minerals (Lalitha and Dhakshinamoorthy, 2014).

The fixation of K involves a chemical process that is controlled by the equilibrium between K located in interlayer positions of minerals and that held at planar sites. Clay minerals such as vermiculites, mica, and illite have the greatest ability for potassium fixation, which affects soil-plant K relations and influences effectiveness of fertilization (Jalali and Zarabi, 2006). The main factors affecting K release in clay minerals are chemical composition and particle size (Raheb and Heidari, 2012). While, in moderately weathered agricultural soils, phyllosilicates play a vital role in releasing of fixed/structural K. The ability of primary soil minerals to release K generally follows the sequence: trioctahedral micas (muscovite) > dioctahedral micas (biotite) > K feldspars (Simonsson et al., 2007).

The most novel method thus far which has been used to assess soil status of K availability has been quantified and characterized based on the method introduced by Beckett (1964a) on the quantity- intensity (Q/I) characteristics, which also assists with investigating potassium-calcium exchange reactions in soils. The Q/I relation can be used to predict K availability to plants in which K^+ in the soil solution (intensity factor I) is related to the changes in exchangeable K^+ in the soil (quantity factor Q). Normally the Q/I curve assists in extrapolating parameters which provide useful information for understanding K^+ availability and can be further used for K^+ fertilizer recommendations. Several authors have made fertilizer recommendations based on Q/I parameters for different field practices. Studies done by (Zhang et al., 2011) reported that, the depletion of K in soil solution by crop removal decreased the equilibrium activity ratio for potassium (AR_e^K) and labile K (K_L) while increasing potassium buffering capacity (PBC^K). Therefore, implication of this study might have effect when making

fertilizer recommendations, hence resulting to successive required fertilizer K as a results of higher PBC^k values signify that more fertilizer will be needed to adjust soil test values (Saleque et al., 2009).

Soil testing procedures for fertilizer K recommendations is an indispensable part to correcting possible K deficiencies through estimating test value of the 'available/extractable K. Different extraction methods are used to extract the varying amounts of K in soil fractions as associated with differences in their chemistry of reagents. Soil testing helps in identifying the optimum level of soil test K required for specific plant growth during soil test crop response calibration phase and after correcting for deficit and factoring potassium requirement factor (KRF) then fertilizer recommendations can be made (Grewal, 2017). The potassium requirement factor, is defined as an appropriate amount of fertilizer K required per ha to raise the test K by one unit in a particular soil (Johnston et al., 1999), and it plays a crucial role when making fertilizer recommendations. The review will focus on soil potassium dynamics, the potassium quantity/intensity relations for determining soil K status, including the use of potassium soil test.

2.1.Forms, Release and Fixation of potassium

Potassium (K) availability determines crop growth and can be understood by taking into consideration the different forms of potassium existing in soils. Soil K fractions consist of solution K (readily available), exchangeable K (available) , non-exchangeable K and are said to be in equilibrium with each other (Johnston and Goulding, 1990). The equilibrium among the three fractions is expressed via SRL. Solution K and exchangeable K are readily available while reserve-K is said to be slowly-available (Sparks, 2001). Structural K, because of the low solubility of minerals, is generally considered limited in soil systems (Brady et al., 2008).

The equilibrium reactions amongst these four different fractions along with ternary exchange involving Ca and Mg determine whether K added will be leached into lower horizons, extracted by plants, converted into unavailable forms or released into available forms, factors which are necessary for predicting fertilizer K recommendation (Sparks and Carski, 1985). Soil solution K can range between 2 to 5 mg K/L in most agricultural soils of humid regions and is mostly higher in arid regions, depending on an extractant used (Haby et al., 1990). This form of K is usually taken up directly by plants through mass flow and diffusion along the concentration gradient and is positively correlated with clay and silt and negatively correlated with sand. Factors such as fertilization and wet-drying changes affect their quantity.

Interrelations of soil pools give a good indication of availability and dynamics of K in the soil system (Figure 2.1). The exchangeable K constitutes approximately 90% of available K and is held by negative charges on clay particles (Sparks and Carski, 1985). This fraction is available to plants but can be quickly exchanged/replaced by other cations in solution. It gives the best indication on the potential K supplying power of soil and is used for making fertilizer recommendations to crops (Sharma and Paliyal, 2015). Non-exchangeable/fixed K is the fraction that is found in weathered micas and vermiculites and trapped between layers of expanding lattice clays and not readily available to plants. The fixed K is influenced by greater binding forces occurring between K and clay surfaces than hydration forces between individual K^+ ions, causing slow releases of K (Lalitha and Dhakshinamoorthy, 2014).

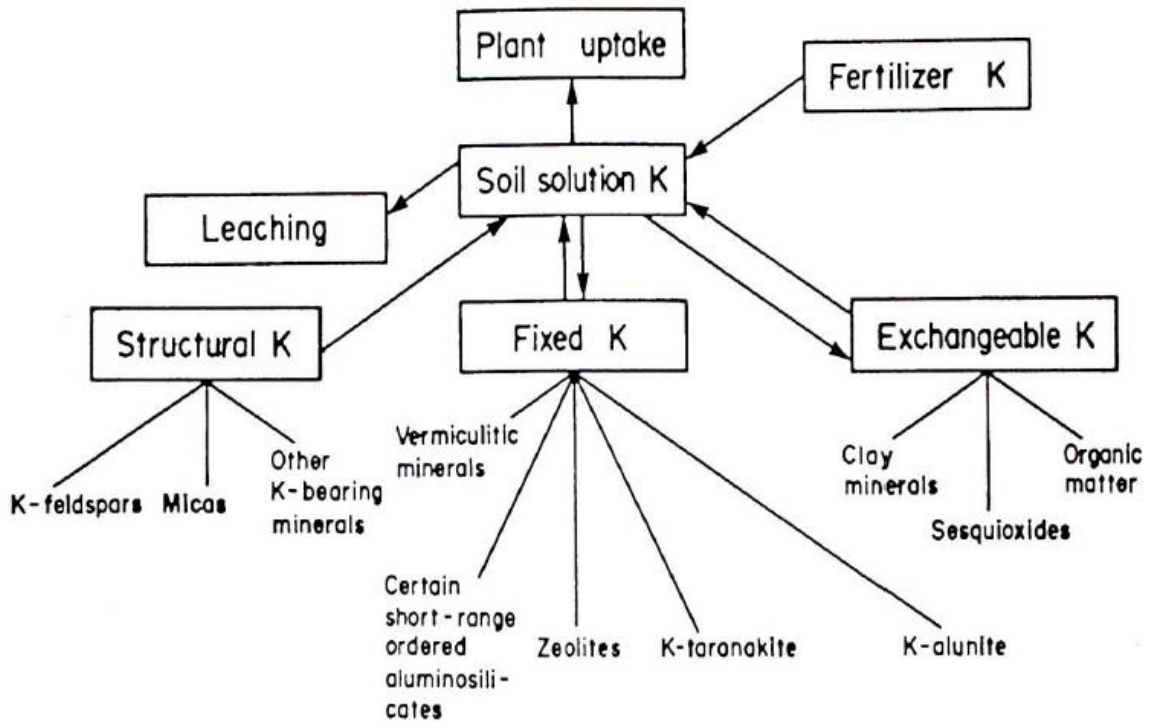

Figure 2.1: Interrelationships of various soil K forms (Sparks and Carski, 1985).

Structural K, a major form of K where 90% of total K is found, exist as part of mineral structure is fixed and not exchangeable(Sparks and Carski, 1985). Clay minerals such as illite, feldspars, and micas are sources of vast amounts of structural K. However, the dynamics of potassium in soil depend on the magnitude of equilibria amongst various forms and mainly governed by the

physicochemical properties i.e acidity, clay content, orgnaic matter and cation exchange capacity of soil.

It is essential to understand mechanisms involved in the release and fixation of K in the soil for long-term sustainability of cropping systems and their effect on K availability (Simonsson et al., 2009). Soils differ extensively in their ability to fix and release K due to differences in quantity and nature of clay, mineral composition, cation-exchange capacity, soil reaction, free lime, organic carbon and amounts of added K fertilizer (Dhaliwal et al., 2006). The release of fixed/ structural K in moderately weathered agricultural soils is mostly influenced by phyllosilicates. The main factors affecting K releases in clay minerals are chemical composition and particle size. The ability of soil minerals to release K generally follows the sequence: trioctahedral micas (muscovite) > dioctahedral micas (biotite) > K feldspars (Simonsson et al., 2007).

The distribution and fixation of K added in soils, amongst the different forms is mostly not homogeneously distributed in soil, due to amount in soil closely related to parent material, degree of weathering, K gains through fertilizer, surface charge density and degree of interlaying of clay minerals (Lalitha and Dhakshinamoorthy, 2014). Weathered micas, montmorillonite, and vermiculite are the main clay minerals responsible for K fixation. The increases in pH between 5.5-7.0 enhance further K fixation in soils, probably as an indirect result of a reduction in hydro aluminum (AlOH). A decrease in K fixation occurs at low pH due to larger numbers of H_3O^+ group in interlayers of clay minerals. Dioctahedral vermiculites are said to play a role in fixing K under acidic soil conditions, while montmorillonite fixes K effectively under dry conditions. Martin et al. (1946) reported that soils with pH values below 2.5 showed no significant K fixation, while the amount of fixed K increased rapidly between pH 2.5-5.5. Potassium fixation characteristics of soils are of utmost importance for evaluating the transformation of fertilizer K in soils and further refinement of fertilizer recommendations.

2.2.Evaluating extraction methods for estimating extractable potassium and requirements in soil

2.2.1. Soil K test methods

Soil testing has been widely used as a diagnostic tool to crop production systems to evaluate plant potassium (K) and other nutrients availability. The estimation of exchangeable K involves extraction of exchangeable K using chemical solutions. However, depending on the solution used, varying amounts of K in soils are extracted (Barbagelata, 2006). The choice of method

for soil K status in soil system is without interferences, due to larger portion of soil K available for plants being held as readily exchangeable K (Thompson, 1995). Extractants that extract multi-elements are convinient and economical for soil testing as they allow simultaneous analysis of several nutrient elements such as Ca, K, P, Mg, Na, Cu, Zn . The most commonly used extractants are given on Table 2.1. In South African soils commonly Mehlich No.3 (Mehlich, 1978), modified Ambic method, Bray No.1 & 2 (Bray and Kurtz, 1945), Olsen (Olsen, 1954) and 1M ammonium acetate(NH_4OAc) (Pratt, 1965) are used.

The main objective for soil K tests is mainly to determine optimum soil test K concentration required for plant growth. Soil K tests further plays a fundamental role in rectifying potassium (K) deficiencies problems in soil through (i) determining the actual content of labile soil K level based on a specific selected extractants, (ii) further assessing soil K deficit from the known optimum level applicable to the crop in terms of the soil K test (Johnston et al.,1999).

Table 2.1: Summary of extractants commonly used for the determination of availability of potassium in soils (Haby et al., 1990).

Extractant name (s)	**Extractants composition**	**Solution pH**	**Soil : Solution ratio**
Ambic K	0.25M NH_4HCO_3 0.01M NH_4F 0.01M NH_4EDTA	8.3	1:10
Ammonium acetate	1M CH_3COONH_4	7.0	1:10
Bray No.1 & 2	0.025M or 0.1 M HCl 0.03M NH_4F	2.6 / 1.0	1:7
Mehlich 3	0.015 M NH_4F 0.2 M CH_3COOH 0.25M NH_4NO_3 0.013 M HNO_3 0.001 M EDTA	2.5	1:10
Olsen	0.5M $NaHCO_3$	8.5	1:20

The K levels are considered to be optimal for plant growth when there is no plant growth responses to additions of K, this is determined during soil test crop response calibration.

However, each extraction method can extract varying amounts of K in soil fractions because of differences in the chemistry of reagents and extraction methodologies involved (Johnston et al., 1999), mainly the quality of the extractant is judged based on its correlation with crop response**.** The following sections provides an overview amongst the three-studied soil test K methods: Ammonium acetate (traditionaly and commonly used method for bases), Mehlich-3 (multiple element extration method that is currently proposed by the Fertilizer Society of South Africa to be used standard K extractant for all South African laboratories), and Bray No.2 (This extraction test extracts acid soluble and adsorbed or available and reserve phosphates present in the soil) (White, 2019)

a) Neutral Ammonium acetate (NH_4OAc)

The neutral 1M NH_4OAc at pH = 7 is the recommended procedure used for exchangeable soil K estimation and further provides the basis for fertilizer recommendations. It is also used to extract exchangeable (Ca, Mg and Na) and to estimate the cation exchange capacity of soils (Brown et al., 1988). Many studies that have been done on NH_4OAc extraction of K gave good estimation of K available to crops as well as most of the K fertilizer recommendations are based on exchangeable K (Jalali, 2007). Zhang et al. (2017) reported that correlation coefficient (r^2) between soil extractable K derived from using ammonium acetate and the relative dry matter response of wheat to K fertilizer was r^2= 0.56 and the method was also best able to predict plant uptake at r^2=0.57. Soil sample drying has been recognized to influence the amount of soil K extracted by the method (Barbagelata, 2006). In the extractant, the available NH_4^+ ions supply a sharp rapid displacement of K from the exchange complex. However, the interactions between soil properties and environmental conditions have influenced the reliability of using ammonium acetate as a soil K test method.

b) Mehlich-3

Mehlich-3 is widely used in most laboratories due to its ability to extract both cation and anions, for soils with varying physicochemical properties. The method is mostly used in the Eastern and Southern states of the United States, where soils are predominantly acidic or neutral in reaction. However, there is still uncertainty about the suitability of the Mehlic-3 on soils that are neutral to alkaline and contain free calcium carbonate ($CaCO_3$) (Schmisek et al., 1998). Mehlich-3 has shown to be most favourable soil test K method in most research. Several investigations have reported that the Mehlich-3 remove almost similar amounts of K as 1M NH_4OAc from soils. Studies conducted by Mehlich (1984) have shown that Mehlich-3 extractant gives values for K that are similar but slightly lower than neutral 1M NH_4OAc with

a correlation coefficient ($r^2 = 0.975$). Studies done by Hanlon and Johnson (1984) reported that neutral 1M NH_4OAc method resulted in much higher amounts of K than Mehlich-3 from a control soil with variability being low with high correlation ($r^2 = 0.998$). However, in studies done by (Eckert and Watson, 1996) the two procedures Mehlich-3 and NH_4OAc showed similar levels of K. High correlations have been obtained between NH_4OAc and Mehlich-3 for soils of the north-central region of the USA (Barbagelata, 2006). Both extractants have NH_4^+ ions in their composition and primarily measure concentrations of exchangeable K in the soil. (Schmisek et al., 1998) reported that when comparing the use of Mehlich-3 and 1M NH_4OAc procedure, linear regression provided a good fit of ($R^2 = 0.94$). Matula (2009) extracted K with water, NH_4OAc, and Mehlich-3 from 36 soils and obtained extracted K 8-212, 82-831 and 89-1032 mg/kg, respectively. The Mehlich-3 method is being investigated for routine use by all South African laboratories for advisory purposes.

c) Bray No.2

The test method makes use of a diluted strong acid plus complexing ions. This extraction test extracts acid soluble and adsorbed or available and reserve potassium present in the soil (White, 2019). Regarded as a standard routine method for determining phosphorus and can also be an alternative use for potassium soil status prediction. The method hold advantage in being able to determine K simply because lower acid concentrations and would then affect lower replacing power of K.

The Bray I and Bray II extraction test proposed by Bray and Kurtz (1945) are suitable for moderately to highly weathered soils of low to medium CEC. And not suitable for soils with a high degree of base saturation, silty clay-loam or finer textured soils with a pH>6.8, soils with a calcium carbonate equivalent of >7 % or soils with large amounts (>2 %) of lime (Sims et al., 1998; Pierzynski, 2000). (In a study done by Ballard (1978) mean amounts of K extracted from various soil groups by NH_4OAc and both Bray test methods showed similar values (closely correlated). The correlation suggests the Bray methods extract essentially the same fractions of K as in NH_4OAc. Hanlon and Johnson (1984) showed that mean soil K values extracted using the Bray No.1 method were 19% lower than the NH_4OAc. Therefore, the question of cation concentration and cations species in the displacement of exchangeable K from the soils is very important when comparing differences between methods.

2.2.2. Predicting the potassium requirement factor

The potassium requirement factor (KRF) is determined through incubation followed by extraction with a specific soil test designated for potassium. The KRF is a specific soil factor

that represents the amount of K required per ha for a unit increase in K levels for a specific soil test and allows for improved K fixation on K recommended for that soil. Due to the time consuming and laborious nature of determining KRF laboratories in KwaZulu-Natal use single KRF values, particularly 2.5 for Cedara and 3.0 for South African Sugar Research Institute (SASRI). However, this assumption assumes that for every 2.5 or 3.0 kg/ha of K this will impact to one unit increase in soil test values depending on an extractant used.

For the approach of determining and using KRF in fertilizer recommendations to be successful, the depth of fertilizer incorporation, as well as any K sorption impact when predicting the nutrient potassium requirement factor, should be considered and this are reflected during the process of incubation (Johnston et al., 1999b). Similarly, the response to K fertilizer applied differs significantly, due to variable responses of crops to applied K and different K adsorption characteristics of different soil types. However, to calculate the nutrient requirement factor such equation has been adapted widely:

K requirement (kg/ha) = (optimum soil K – measured soil K) x KRF

The variability in soil properties and clay mineralogy are the most important properties that determine KRF (Johnston et al., 1999a). The process of determining KRF is laborious and cannot be routinely adopted for a specific soil, the process involves (i) a six weeks (42 day) incubation with alternate cycles of wetting and drying after addition of K at increasing rates, (ii) the extraction of K using appropriate extraction methods, followed by (iii) plotting the amount of K recovered in the extraction solution against added K. The relationship generally gives a linear regression function. Most soil testing laboratories are faced with the difficulty of dealing with soil types that vary not only in texture but also in clay mineralogy, but also the time consuming and laborious nature of determining KRF. Nonetheless this does not diminish the value of this method especially for understanding K behaviour.

Elephant and Miles (2016) reported that the KRF values over a wide range of soils of the South African sugar industry, KRF varied from 1.56-7.73 kg K/ha/per unit soil test, using AMBIC extract (NH_4HCO_3/NH_4F/EDTA), an extractant which is more popular in KZN province. Johnston et al. (1999) established that the K requirement factor, of a wide range of KwaZulu-Natal (South Africa) soils varied between 1.5 and 8.8 kg K/ha/per unit soil test using AMBIC extract (NH_4HCO_3/NH_4F/EDTA). They also reported poor correlation between KRF and routinely measured soil parameters and suggested that to be largely due to the fact that KRF was strongly related to the mineralogy of layer silicate minerals, particularly vermiculites and

weathered micas. Johnston et al. (1999b) reported that soils with KRF values greater than 4.0 kg/ha have a definite presence of vermiculite in the clay fractions.

However, the incubation procedure of 42 days through determining KRF is time consuming, and thus cannot be adopted for routinely purposes The other weaknesses associated with KRF values in making fertilizer recommendations is that KRF fails to provide indication of how much fixed K will become available to a crop in each season, given that the crop factor is not accounted for. Therefore, certain measures need to be accounted for such time consuming methodology involving incubation studies. This can be achieved through use of empirical functions, a process which can be likened to infrared spectroscopy. A study by Johnston et al. (1999) showed that for KRF prediction from routinely measured soil properties was unsatisfactory. Alternative techniques are needed to determine soil specific KRF such as FTIR. Attempts have been made to use routinely measured soil properties and mid-infrared spectroscopy (MIR) on the future of soil testing to predict KRF values. These may play a vital role in providing fast and reliable KRF results. Studies by (Elephant et al., 2019) were able to evaluate and prove MIR ability in assessing capacity to predicting KRF. Moreover, Mid-infrared spectroscopy (MIR) has been reported to accurately predict soil nutrient buffering capacity (Towett et al., 2015).

2.3.The future use of mid-infrared (MIR) spectroscopy to effectively predict potassium requirement factors.

Surrogate methods such as infrared spectroscopy, by their nature tend to predict soil properties simultaneously (Janik et al., 2009 ; Rossel et al., 2016). Fast and convenient soil analytical techniques are required for soil quality assessment. The use of Mid-infrared diffuse reflectance spectroscopy can effectively provide rapid, cheap, and simultaneous predictions for several soil properties compared to the use of conventional methods. Use of MIR spectroscopy is non-destructive and improves the preservation of the integrity of soil sample. Other advantage of using MIR is that a single spectrum allows for the simultaneous prediction of numerous soil chemical and physical parameters. This technique is expected to revolutionise soil testing, including testing for soil K. (Rossel et al., 2006) on the use of MIR demonstrated that MIR can simultaneously analyse for pH_{ca}, organic carbon, clay, cation exchange capacity, exchangeable (calcium, aluminium and potassium), available phosphorus, and electrical conductivity with varying accuracy. Moreover, MIR does not require the use of expensive chemical extractants which might be time-consuming, as conducted through incubation

procedures. Due to these reasons MIR is more efficient in the analysis of large number of samples and soil properties from a single spectrum, compared to conventional wet chemistry methods (Siebielec et al., 2004).

Infrared spectroscopy involves the use of different multivariate calibration methods and chemo-metrics for calibration and validation, which assists in evaluating the performance and accuracy of using MIR spectroscopy (Cao, 2013). The quality of the calibration is evaluated using coefficient of determination (r^2) and the ratio of prediction to deviation (RPD). The quality of IR calibrations ranges from poor (low r^2 and RPD values) to excellent. The quality of the calibrations are most likely affected by the spectral region, multivariate method, calibration range, number of samples used, and the reference method used to measure exchangeable K. Frequently the partial least square fit (PLS) is used as a regression model to data that has degree of covariance in the independent or predictor variable, the method also assumes that systematic variations observed in the spectra are a consequence of the concentration change of the components (Taylor et al., 2009).

The calibration of the MIR-based approach to predict KRF in soil could provide a cheaper and time-effective method compared to conventional chemical procedures, especially where large numbers of samples need to be analysed routinely as the case in fertilizer advisory services and commercial laboratories. Therefore, feasibility of MIR to predict KRF in soil should be fully investigated.

2.4.Quantity-intensity relations of potassium in soils

Quantity-intensity (Q/I) relationships is considered to provide the most comprehensive information regarding K availability compared to soil K tests. The Q/I relation can be used to predict K availability to plants in which K^+ in the soil solution (intensity factor I) is related to the changes in exchangeable K^+ in the soil (quantity factor Q) (Hosseinpur and Tadayon, 2013). The Q/I relationships was initially proposed by Beckett (1964a, b) and are based on Schofield's Ratio Law. One other advantage of the approach is that it able to predict the relationship between these two parameters for soil K status through evaluating the K-(Ca+Mg) exchange equilibria. The potassium Q/I relations are more theoretically justified in terms of their parameters for further fertilizer K management as illustrated (Figure 2.2).

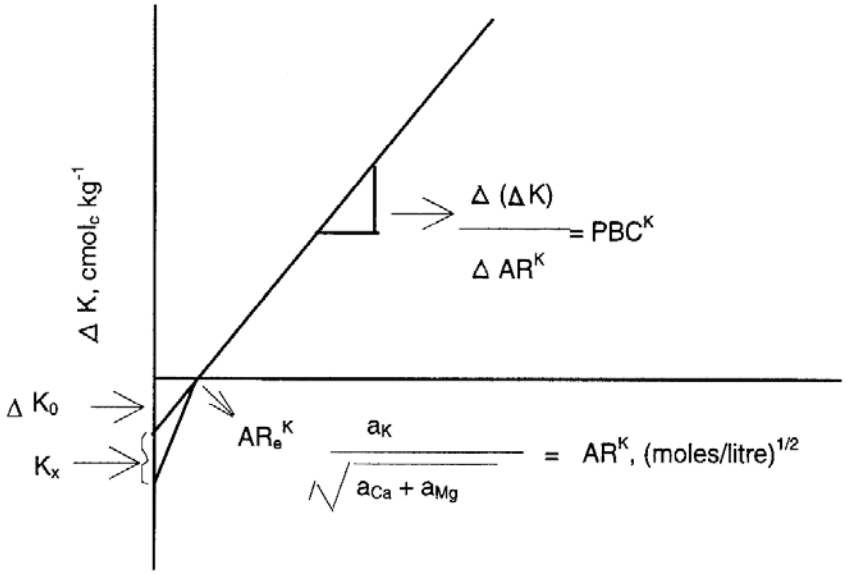

Figure 2.2: Quantity-Intensity (Q/I) plot illustrating three parameters evaluated

The parameters obtained from Q/I curves signify the following components: The specific K adsorption sites (K_x); the measure at which soil gains or loses potassium (ΔK) usually restricted in sandy soils and more in clayey soils are obtained by subtracting the value where the curvilinear line intersects the y-axis from ΔK^0; equilibrium activity ratio for potassium (AR_e^K) labile K intensity measure, represents the intercept of the curve on the x-axis. The labile or readily exchangeable K (ΔK^0) is obtained by extrapolating the linear part to intersect the y-axis, greater values indicates greater release into soil solution resulting into larger pool of plant-available K. The potential buffering capacity of K (PBC^k) is represented by the slope of the curve.

Potassium Q/I relations play massive role in predicting K^+ availability to plants and to understanding and evaluating K^+ fertility status of soils (Shenker and Seth, 2018). The equilibrium activity ratio is said to be the measure of the availability or intensity of labile K in the soil and represents the K that is immediately available to crop roots (Yawson et al., 2011). According to (Beckett, 1964b) lower AR_e^K values indicates reduced amounts of potassium for plant uptake and lower exchangeable K levels. The AR_e^K values <0.001 (mol/l) $^{0.5}$ imply that K^+ is absorbed at high affinity (specific) sites whilst values which are >0.01 (mol/l) $^{0.5}$ K^+ is absorbed on planar sites as reported by (Sparks and Liebhardt, 1981). Labile K parameter represents a measure of the exchangeable K in soil which during period of equilibration between soil solids further enhances the ion exchange (Zarrabi and Jalali, 2008). Higher values

of the labile k are said to influence greater K^+ release into soil solution causing impact to a larger pool of labile K also being available (Sparks and Liebhardt, 1981).

The potassium potential buffering capacity (PBC^K) which is amongst the Q/I parameters, describes the soils capacity to resist changes in the content of available potassium influences K availability and fertilization. (Le Roux and Sumner, 1968 ; Zharikova, 2004) concluded that PBC^K values are divided into very low those less than 20 cmol/kg $(mol/l)^{0.5}$ and high those that are greater than 200 cmol/kg $(mol/l)^{0.5}$.High values of PBC are associated with a good availability of K, whilst low values indicate a need for fertilization (Le Roux and Sumner, 1968 ; Hamed and Amin, 2017).Various factors in the soil system tend to influence the buffering capacity i.e. (i) charge density of the surface, (ii) characteristics of the surface and (iii) the available surface area for ion exchange (Hosseinpur and Tadayon, 2013). The property varies which changes with changes in intensity and capacity factors of soil K and, therefore, indicates the ability of soil to maintain the intensity of K in solution. In terms of fertilizer application, high PBC^k values signify that more fertilizer will be needed to adjust soil test values (Saleque et al., 2009).

Several studies have been done based on the above decribed Q/I parameters in which they relate it with fertilizer application and ability of K availability being affected. However, (Beckett and Nafady, 1968) concluded that potassium buffering capacity and K_x are less influenced by K fertilization. Beckett (1964) reported that there is an effect of fertilizer addition on Q/I relations on Beaufort Shale soil, former Natal, since fertilizer addition increased exchangeable K forms and activity ratio while potential buffering capacity remained unchanged with K additions at different treatments. A study that was conducted in Argentina (De la Horra et al., 1998) to modify Q/I parameters on four agricultural soils through K addition in an incubation trial, simulating K fertilizers application. Amongst the four soils, two showed increase in labile forms of K, which were proportional to the amount of added K, due to different fixing capacity of the soils, related to the clay content and mineralogical composition. While the addition of K produced proportional increases in AR_e^k and ΔK^0 values. This was attributed to the presence of non-saturated planar sites at the highest rates of K applied (De la Horra et al., 1998). This suggest that the above mentioned parameters which provide useful information for understanding K^+ availability in soils and maybe used for K^+ fertilizer recommendations are poorly understood. However, studies assessing equilibrium activity ratio as governed by the Schofield ratio law to fertilizer recommendations are lacking and certain approaches need to

be undertaken to fully substantiate effect of ratio law in improving fertilizer K recommendations. The KRF values supposedly should correlate with PBC as determined via Q/I relations, Q/I relations theoretically provides the most comprehensive information with regards to K dynamics, given that the methodology is based on equilibria concept as experimentally established by Schofield. Nonetheless Q/I assume a conformation to the ratio law, and as outlined by Schofield the conformation is subject to surface charge characteristics, there are limited studies on these parameters.

2.5.Fundamentals of K-equilibria on Ratio Law

Soil potassium and calcium and their availability to plants in conditions where they are not at limited state are controlled by amounts and forms of combination of ions in the solid phase (Beckett, 1964b). Due to ion exchange principles K exchange with various other metal cations on the clay surface, given that Ca is mainly the dominant cation on the exchange sites, it is assumed that K availability is governed by its exchange with Ca at equilibrium and as such Ca-K binary exchange have been widely used. Therefore, it is of the utmost value to measure the relation between K and Ca. In the past, many attempts have been made to develop theoretical laws governing the distribution of cations between the solution and the adsorbing complex in the soil. Soil processes involving ionic nutrients have been investigated through the Schofield Ratio Law (Schofield, 1947a).

The ratio law, states that the activity ratios of potassium to that of (Ca + Mg) treated as single unit $(a_K/(a_{Ca+Mg})^{0.5}$ of solutions in equilibrium at a given clay colloid with a complement of exchange cations are independent of their concentrations. The activity ratio measures the instant available potassium in soil systems. The law depends mostly on the exclusion of anions from the inner parts of the diffuse double layer around colloid particles (Schofield, 1952). Several studies have been reported where soils do not conform to ratio law. Taylor (1958), when evaluating ion pair K-(Ca+Mg), reported that two out of four soils did not conform to the law while those that strictly obeyed the law did so on low potassium status. Conversely, on their study based on K-Ca exchange isotherm for kaolinite Beckett and Nafady (1967) concluded that at low pH exchangeable ions, which are associated with edge sites with excess negative charge obeyed the ratio law, while those associated with planar surfaces with positive charges did not obey the law. Le Roux (1966) investigated a variety of Natal soils and found that the ion pair of K-(Ca+Mg) fully conforms to the Ratio law.

Numerous conditions are required for the Law, such that the given soil should maintain fixed quantities of labile K and Ca as soil exchange ion within solution then the free energy of exchange should be independent of changes in the concentration and composition of the soil solution. For the Law to be fulfilled the chemical potentials of the two ions should depend only on their amounts and not affected by changes in the solution. Therefore, for this condition to be applicable (Schofield, 1947a, 1952), almost all the labile forms of the two cations must be attached inside or inner part of the diffuse layer of cations surrounding the negatively charged surfaces of the soil with no changes in concentrations. The law could not be applicable when the concentration of the soil solution is high enough for anions to penetrate to the inner part of the double layer.Usually soils of which its known or suspected that the exchange surfaces bear significant properties of positive charges would unfortunately not conform to the ratio Law (Beckett, 1964b). The central role of the Ratio law is that it provides a method of measuring relative values of the K solid phase. The activity ratio as a measure of the difference between the chemical potentials of two ionic species in the soil system is said to be theoretically independent of the soil solution concentration under normal circumstances (Schofield, 1947a). Therefore this implies that the activity ratio values do not only depend upon potential K in the soil but also depend upon Ca and Mg potential in the same soil. Surface charge properties are therefore crucial in conformation or lackthereof on ratio law.

2.6.Surface charge in soils

Surface charge tends to control a wider range of physicochemical reactions in soil system, especially the retention of exchangeable cations and anions (Moghimi et al., 2013). The charge of soil particles surfaces affects adsorption, dissolution, and colloidal reactions in general. Processes which influence transport and fate of solutes, including K^+ ions. Electrochemistry at the surface of colloidal particles in the soil system is mostly impacted by physical and chemical phenomena such as dispersion of soil particles, cation-exchange capacity, anion adsorption and pH variability (Ribeiro et al., 2012). Electrical charges on their surfaces of most common soil minerals are either permanent, because of change deficits in their structure, or are temporary impacted by specific sorption of potential determining ions (H^+ and OH^-). However, the sign and magnitude of electrical charge usually depends on soil solution pH (Sposito, 2008). The pH of a suspension medium at which colloidal particles have no surface charge is termed point of zero charge (PZC). The point of zero charge corresponds to the point at which sufficient amounts of potential-determining ions (H^+ and OH^-) are adsorbed by the soil regardless of

electrolyte concentrations (ionic strength, I), but rather that there are equal amounts of positive and negative charges (Sakurai et al., 1988).

The determination of PZC for ion-exchanging colloidal particles is crucial, in that it plays an important role in understanding effective adsorption processes in the environment (Miyittah et al., 2016). The PZC is a fundamental property used for full variable -charge surface determination. The parameter enables further soil response predictions to changes in surrounding conditions such as fertilizer application in the field (Sakurai et al., 1988). However, various methods have been proposed for PZC characterization in soils and other materials of variable surface-charge. Methods are developed considering differences in electrolyte solutions. Such methods are differentiated to potentiometric titration (PT) which assess changes in surface potential with changes in the activities of H^+ and OH^- at different $^-$, salt titration and salt titration-potentiometric titration (ST-PT) (Tan et al., 2008). The point of zero net charge (PZNC) in soil environments, particularly corresponds to surface charge which will carry net negative charges. In conditions where pH of a soil is above its PZC the soil surface and such will result in net negative charge on the soil surface , whereas pH below PZC exchange of one negative ion for another will occur influencing soils to retain anions electrostatically (Appel et al., 2003). However, the PZNC is extrapolated when the cation exchange capacity (CEC) and anion exchange capacity (AEC) crossover (Figure 2.3).

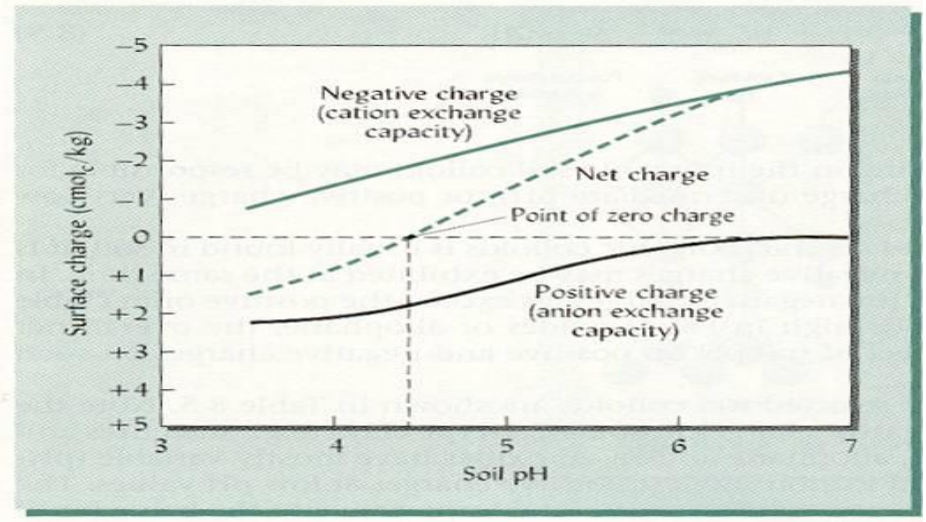

Figure 2.3: Schematic relation between AEC, CEC and net surface charge in determining the PZNC (Source:(Brady and Weil, 2002))

The cation exchange capacity is defined as a measure of negative charge of a material that can be neutralized by exchangeable cations, plays a vital role in enhancing soils ability to holding

and exchanging nutrients (i.e. NH_4^+, Ca^{2+} and K^+) . In contrast anion exchange capacity (AEC) measures the soils ability to retain anions such as phosphate (Brady and Weil, 1984). Furthermore, the parameter (PZNC) is said to involve measurement of retention for indifferent cation (Na^+, Li^+, K^+ and Ca^{2+}) an anion (NO_3^- and Cl^-) as a function of the solution pH at a fixed ionic strength a modified method of (Marcano-Martinez and McBride, 1989). Several soil constituents such as phyllosilicate minerals, iron and aluminium oxides and organic matter, are the most electrochemical attributes that influences the point of zero charge. The oxides frequently contribute to increasing the net positive charge and PZC in soils, whereas phyllosilicate minerals and organic matter increase net negative charge while reducing PZC (Ribeiro et al., 2012). Whereas highly weathered soils which are mostly dominated by 1:1 clay mineral especially kaolinite and iron and aluminium oxides may cause severe changes on sorption of cations and anions and organic compounds on the soil surfaces.

2.7.Conclusion

In this review, methods to evaluate potassium status and the factors which affects potassium dynamics and potassium equilibria were discussed. The evaluation of the potassium requirement factor using three extractant would play a massive role in predicting the most suitable method for further potassium fertilizer recommendations. However, the determination of the KRF is based on the laborious incubation method over a period of six weeks. The review indicates the need to evaluate potassium Q/I relation parameters especially those that might influence potassium fertilizer application. The soil charge characteristics is reported to affect physicochemical reactions, especially during ion adsorption.

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CHAPTER THREE: METHODS AND MATERIALS

3.1. Soil sampling and preparation.

The samples were collected from various regions of KwaZulu-Natal (i.e. Pietermaritzburg, Mooi-river, Bergville, Wartburg, Underberg and Richmond) to cover a whole range of different soil properties by including differences in land uses (pasture, arable, natural and semi-natural vegetation), parent material differences were negligible. The 42 topsoil samples were collected from the 0-20 cm depth, air dried on polystyrene trays, and ground to pass through a 2mm sieve. Soils were grouped according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014) and the South African soil classification names (Soil Classification Working Group, 1991). The soil groups of WRB and soil forms of Soil Classification Working Group are represented in Table 3.1.

Table 3.1: Soil sample classification used in this study.

#WRB	***Soil type**	**Total number of samples**
Acrisols	Tukulu	**1**
Ferralsols	Clovely Griffin Hutton Kranskop Pinedene	**18**
Fluvisols	Dundee	**2**
Leptosols	Cartref Glenrosa Mispah	**5**
Luvisols	Bonheim Sepane Swartland Katspruit Willowbrook Inanda	**6**
Nitisols	Shortland	**2**
Plinthosols	Dresden Kroonstad	**7**

	Westleigh	
	Wasbank	
	Longlands	
Vertisols	Rensburg	**1**

[#]International classification systems (WRB reference group)

[*]Soil types are according to South African Soil Classification System.

3.2. Soil characterization.

General soil characterization was carried out by KZN Department of Agriculture and Rural Development's fertilizer advisory services laboratory (Cedara). Sample density (g cm^{-1}) was determined based on the mass/volume of airdried soil sample of a 10-ml (10 cm^3) scoop of a dried and milled soils. Soil pH, in 1 *M* KCl and deionized water (1:2.5 soil: solution), was determined electrometrically using a standard glass electrode. Ten ml of soil was scooped into a 50 mL plastic beaker before the addition of 25 ml of HCl solution. The suspension was stirred and allowed to stand for 30 minutes before the pH was measured.

Exchangeable K were extracted by ammonium bicarbonate EDTA, while Exchangeable Ca^{2+}, Mg^{2+} and acidity were measured in bulked samples following methods described by Manson and Roberts (2000). Approximately 2.5 ml of soil was scooped into sample cups, 25 ml 1 M KCl solution added, and the suspension stirred at 400 r.p.m. for 10 minutes using a multiple stirrer, before filtration through a Whatman No.1 filter paper. Five mL of the filtrate was diluted with 20 ml of 0.0356*M* $SrCl_2$, and K, Ca and Mg determined by atomic absorption spectrophotometry (Varian 2600). To determine extractable acidity, 10 mL of the filtrate was diluted with 10 ml of deionised water and 2-4 drops of phenolphthalein added and titrated with 0.005*M* NaOH.

Particle size distribution and total C was carried out in soil science laboratories at the university of KZN. Particle size distribution of the soils was determined using a Bouyoucos hydrometer method after dispersion of soil with sodium hexametaphosphate (Calgon solution) (Bouyoucos, 1962), based on Stoke's Law. Total carbon (C) for each sample (passed through 0.5 mm) was determined by dry combustion using Leco Auto analyser (TruMac CNS/NS) (Wright and Bailey, 2001).

3.3. Determination of potassium requirement factors

Soil samples (42) were air-dried and ground to pass through a 1-mm sieve. Subsamples of each soil were placed in sealed plastic containers, amended with four levels of K (0, 30, 90 and 120

mg K kg^{-1}) of finely ground potassium dihydrogen phosphate (KH_2PO_4) and incubated at a constant temperature 25°C for six weeks. Adjustment of moisture to field capacity was done at the beginning of incubation through addition of distilled water. Three drying cycles were included by wetting to field capacity every fortnight, this was determined by field capacity determination (using pressure plates). Following incubation, subsamples were air-dried and again ground to pass through a 1-mm sieve. Potassium requirement factor was determined for three different extractants i.e., Mehlich-3, Ammonium acetate and Bray No.2 extraction procedures explained on Table 2.1, followed by analyses using the atomic absorption spectrophotometer (Varian AAS 220). The linear plot of K added, and K measured, gave a linear regression with the slope of the function which then provided the K requirement factor (KRF), expressed as kg K ha^{-1} per mg K L^{-1}. The function represents the quantity of K fertilizer that must be applied per hectare to raise the soil test values by one unit for fertilizer recommendation services (Johnston et al., 1999b). Slopes of all relationships between soil test K and applied K followed a linear pattern (Figure 3.1). The values of KRF were determined from the inverse of the slope for each soil. All analysis was replicated three times.

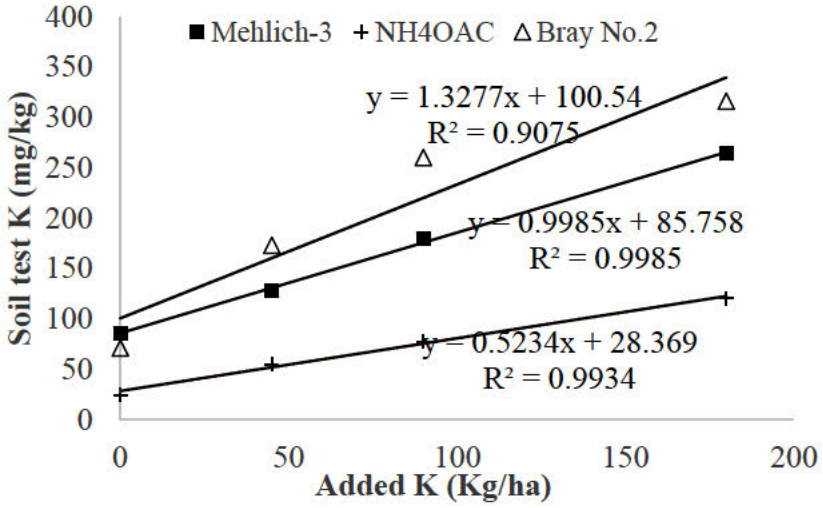

Figure 3.1: Relationship between added potassium and soil test potassium amongst three extractants studied (Nitisol S26).

3.4. Potassium Q/I relations.

The determination of potassium Q/I parameters were selected based on differences in soil groups ten different soil samples to account for differences in soil forms. Five grams of air-dry soil were equilibrated with 50 ml of graded K solutions with a range of 0-200 mg l^{-1} K (0, 10, 20, 30, 60, 160, 200 mg/l K), in 0.01M of $CaCl_2$ as a supporting electrolyte. The contents were shaken on a horizontal shaker for 2 hours and equilibrated for 24 hours, followed by

centrifugation at 400 rpm for 5min and filtered using Whatman No.1 filter paper into a storage bottle. Potassium, calcium, magnesium in supernatant were analysed using atomic adsorption spectrometer (Varian AAS 220). Further, Q/I parameters of studied soils were determined. The K quantity factor (ΔK) was calculated from the difference in the concentration of K^+ in the initial (CK_i) and in equilibrium solutions (CK_f). The activity ratio of potassium (AR^K) was calculated through determining the activity coefficient of an ionic species calculated by using the Davies equation given by (Sposito, 1989). Following equations below were used for (ΔK) and (AR^K) respectively:

Calculation:

$\Delta K = CK_i - CK_f$

$AR^K = aK / (aCa+aMg)^{0.5}$

Where aK, aCa, aMg refer to the activity coefficient of K, Ca, and Mg respectively at equilibrium calculated using Davies equation below:

$\text{Log } \gamma = -0.512Z^2 [(I^{0.5}/1+I^{0.5}) - 0.3I]$

Where Z: the valence charge of ionic species and I: ionic strength calculated as below:

$I = 0.5\Sigma CiZi2$

Further, the ΔK was plotted against activity ratios of K (AR^K) and were constructed for each soil studied to obtain Q/I curves. The linear function assisted with extrapolating, potassium buffering capacity of K (PBC^K) represented by the slope of function, AR_e^K from the x-intercept of Q/I curve where ΔK = 0 and the -ΔK from the y-intercept of the Q/I curves.

3.5. Conformation of soils to Ratio Law.

The method employed was designed in-order to determine over a range of concentrations the activity ratio ($a_K/\sqrt{(a_{Ca} + a_{Mg})}$) of solution. Five gram (5g) of sieved soil was shaken on a horizontal shaker for 30min in three 50 ml aliquot solutions 0.002M, 0.006M and 0.01M containing KCl and 0.01M $CaCl_2$ as a background electrolyte for each solution to equilibrate for 12hr. The contents were centrifuged at 400 rpm for 5min and filtered using Whatman No.1 filter paper into a storage bottle. The filtrate was analysed for K (flame photometer), Ca and Mg (atomic absorption spectrophotometry) using the (Varian AAS 220) and assumption of conformation to ratio law was calculated as explained by Schofield (1947b).

Calculation:

Ionic strength: $0.5 (C_{Ca}+C_{Mg}+C_K)$

Where: C_{ca}, C_{Mg} and C_K are the concentrations of Calcium, Magnesium and Potassium.

Activity coefficients: (aCa, aMg and aK)

Log γ = -0.512Z^2 [($I^{0.5}$/1+$I^{0.5}$) – 0.3I]

Where Z: the valence charge of ionic species and I: ionic strength

Activity Ratio: aK /$(aCa+aMg)^{0.5}$

3.6. Soil charge characteristic.

3.6.1. Determination of point of zero salt effect (PZSE).

This was done in 42 soil samples. The method used involved various steps in which 2g soil was added in each of fourteen 50-ml polyethylene centrifuge tubes arranged into two rows of seven. To vary salt concentration levels, 10 ml of 0.1M NaCl to each tube in one row and 0.01M NaCl for the other row. Subsequently, 0.1 M and 0.01M HCl or NaOH were added to obtain a range of pH values (2-6). The tubes were then filled with distilled water to a total volume of 20ml. After closing the tubes, the samples were equilibrated for 4 days at 25°C with shaking for 3 h/day. Then, the pH_1 values (with soil) were measured. The pH_1 values represents the concentration of protons or hydroxyl ions in the supernatant. For the conversion, the ionic activity coefficients were obtained with modified Davies equation (Davies, 1962). The blank titrations (without soil) at the two NaCl concentrations were also carried out.

The adsorbed amounts of H^+ or OH^- at the final pH were calculated from the amount of the HCl or NaOH added to the samples minus the amount of acid or base used by blank titration. The value of ΔH-ΔOH ($cmol_c$/kg) which represent the Point of zero salt effect for each sample at each ionic strength examined was calculated and plotted against equilibrium pH. Under the assumption that NaCl is an indifferent electrolyte, the adsorption curves at the two different NaCl concentrations should intersect at one point; the pH of this point is the PZE (Figure 3.2).

Calculation:

Davies equation:

Log γ = -0.512Z^2 [($I^{0.5}$/1+$I^{0.5}$) – 0.3*I*]

Where ionic strength (I):

$I = 0.5\Sigma C_i Z_i^2$

Calculation point of zero salt effect (PZSE):

$$\Delta H\text{-}\Delta OH = \frac{[10-pHB-10-pHS]-[10-(14-pHB)-10-(14-pHS)]}{\gamma} \times \frac{0.1}{W} \text{ (PZSE)}$$

Where:

ΔH-ΔOH = apparent proton surface charge density calculated by titration at given ionic strength and pH in cmolc/kg,

ΔH = difference between the final H^+ concentration of suspension and that of the blank,

ΔOH = difference between the final OH^- concentration of a suspension and that of the blank,

pH_B = pH of blank solution,

pH_S= pH of the solution equilibrated with the sample (pH_1),

14 = conditional dissociation product of water,

γ= single ion activity coefficient calculated with Davies equation (Davies, 1962) and

W = air-dried soil sample weight (g)

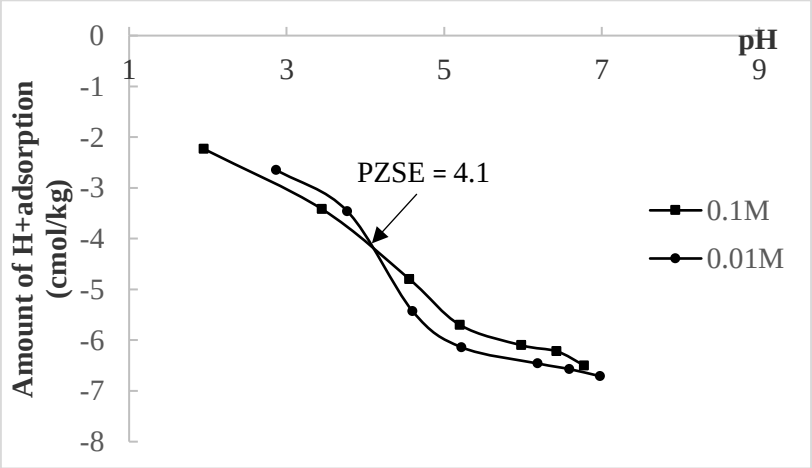

Figure 3.2: Potentiometric titration curves of a selected soil group for illustration as a function of pH at different ionic strengths

3.6.2. Point of zero net charge (PZNC) determination.

Determination of CEC and AEC for charged surfaces as a function of pH was accomplished through the ion adsorption method on all 42 soil samples. Using a method modified by Marcano-Martinez and McBride (1989). Soil (2.5 g) was placed into each 10 pre-weighed 50 ml polyethylene centrifuge tubes to which 25 ml of 1M KCl was added. The samples were shaken in a horizontal shaker for 1 h, centrifuged for 10 min at 200rpm, and the supernatant was discarded. A volume of 25 ml of 0.01M KCl was used to wash the suspension five times, and at the final washing the pH of suspension was adjusted by adding 1M KOH or HCl ranging

from (1-12) to span expected PZNC. The tubes were then shaken on a horizontal shaker for 4h, centrifuged at 400rpm for 5min and pH of supernatant was recorded. The rigorous washing procedure was carried out to ensure exchange sites were saturated with K^+ and Cl^- as a function of pH and I, The suspension was washed four times with 10ml of 0.5M $NaNO_3$ to displace the adsorbed K^+ and Cl^-. Supernatants were stored, and concentration of K^+ and Cl^- were determined by the (Varian AAS 220) and colorimetric (silver nitrate titration) method, respectively. Graphs of CEC and AEC vs pH were plotted and the pH where cation adsorption was equal to anion adsorption is the PZNC.

Calculation:

Following equations for CEC and AEC were used to calculate PZNC.

$$\mathbf{CEC} = \frac{a}{10} \times \frac{1}{39.01} \times \frac{100}{b}$$

$$\mathbf{AEC} = \frac{a}{10} \times \frac{1}{35.5} \times \frac{100}{b}$$

a concentration of potassium or chloride (mg/L)

b mass of dry soil (g).

CEC/AEC (cmol/kg)

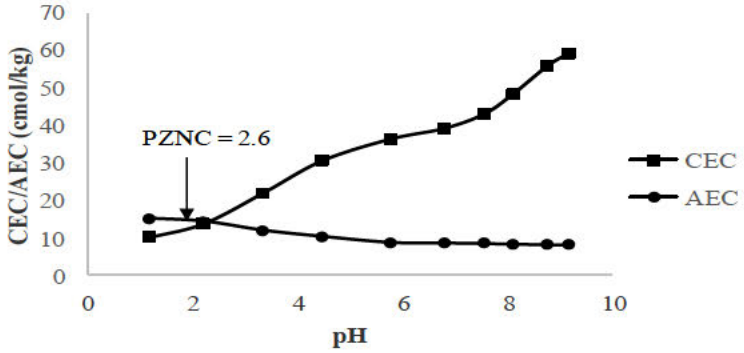

Figure 3.3: Selected soil group illustrating where Point of zero net charge was determined.

3.7. Statistical analysis

Correlations and regression analyses were performed to compare the effectiveness of K requirement factors (KRF) for three extractants (i.e., Mehlich-3, Ammonium acetate and Bray No.2) and also relate it with selected physicochemical soil properties was carried out using Microsoft Excel 2016. Probability tests was performed at level of significance ($P < 0.05$)

CHAPTER FOUR:RESULTS

4.1. Physicochemical properties

The physical and chemical properties amongst the 42 soils in the study overall showed variation. Textural class ranged from mostly sandy, clay loam, to clay with clay content ranging from 6% to 30% (Table 4.1/ Appendix 4.1). The Vertisols had the highest clay content of up to 30.2% with Ferralsols group having lowest mean clay content at 14.70%. Mean total carbon value was highest in Nitisols (5.88%), followed by Luvisols (4.45%) and Vertisols (4.33%) with Leptosols having the lowest at 2.11%. Acrisols showed the highest mean exchangeable acidity values (1.12 cmol L^{-1}), followed by Ferralsols (0.78 cmol L^{-1}) and Fluvisols (0.68 cmol L^{-1}), with Vertisols having the lowest at 0.15 cmol L^{-1} (Table 4.1). The results of acid saturation followed the same trend as that of exchangeable acidity (Table 4.1). The mean values of total cations followed a directly opposite trend to those of exchangeable acidity and acid saturation, with highest in the Vertisols (18.23 cmol kg^{-1}), followed by Nitisols and Luvisols, while the lowest was in the Acrisols (5.47 cmol kg^{-1}). The pH (KCl) ranged between 3.78 and 6.47 a clear representation of acidic to near neutral pH. Luvisols had the highest mean pH (KCl) values with the Acrisols having the least. Sample density mean values amongst the grouped soil samples varied with Nitisols having the lowest and Acrisols and Plinthosols having the highest. Except for some samples of Nitisols and Plinthosols which had sample densities higher than 1.5 g cm^{-3}, all other samples had less than 1.2 g cm^{-3} (Table 4.1).

Table 4.1: Mean values of physical and chemical properties of soils (***n* = 42**). With values of range represented in parentheses. Soil groups (ranges) not presented were undeterminable due to their number of samples.

Soil type	Clay content	Total carbon	Exch.acidity	Total cations	Exchangeable K	pH	pH	Sample density
	%	%	(cmol/L)	(cmol/L)	mg/l	KCl	H_2O	g/ml
Acrisols	15.3	3.01	1.12	5.47	117	4.07	5.74	1.19
	-	-	-	-	-	-	-	-
Ferralsols	14.7	3.96	0.78	5.92	147.8	4.4	5.55	0.99
	(6.06-27.9)	(0.79-7.87)	(0.07-2.19)	(2.52-11.37)	(29.0-521.0)	(4.00-6.37)	(4.85-6.37)	(0.84-1.16)
Fluvisols	14.9	3.04	0.68	8.13	101.5	4.75	5.45	1.11
	(9.17-20.6)	(2.39-3.68)	(0.21-1.15)	(3.85-12.4)	(99.0-104.0)	(4.13-5.36)	(5.39-5.54)	(1.04-1.18)
Leptosols	22.6	2.11	0.45	8.14	145	4.61	5.66	1.1
	(18.34-27.43)	(0.50-3.10)	(0.07-1.41)	(3.01-10.84)	(26.0-227)	4.13-4.93	5.15-6.04	(0.97-1.15)
Luvisols	18.2	4.45	0.31	11.7	88.5	5.1	5.75	1.15
	(10.30-27.3)	(1.84-7.82)	(0.04-1.42)	(2.53-20.76)	(63.0-118)	(2.3-4.17)	(5.03-6.59)	(0.98-1.51)
Nitisols	21.8	5.88	0.41	13.6	161	4.83	5.16	0.98
	(15.20-28.4)	(4.98-6.78)	(0.12-0.7)	(5.76-21.5)	(146-175)	(4.35-5.3)	(5.95-5.96)	(0.91-1.04)
Plinthosols	19.9	2.41	0.49	6.67	185	4.44	5.68	1.19
	(7.18-27.8)	(0.66-3.23)	(0.07-1.71)	(2.49-11.9)	(52.0-578)	(3.78-5.19)	(5.06-6.26)	(0.96-1.86)
Vertisols	30.2	4.33	0.15	18.2	66	4.59	5.38	1.1
	-	-	-	-	-	-	-	-

4.2. Potassium requirement factor as determined by three extractants

The slope of the plot between the added potassium and soil solution potassium extracted by three different extractants gave the K requirement factor (KRF) as expressed in kg K ha^{-1} per unit soil test of soil (Figure 3.1). The mean KRF values for the three extractants are presented in (Table 4.2 and Appendix 4.6). Ammonium acetate had the highest KRF mean values with the lowest for the Bray No.2 extractant. For Mehlic-3 the Luvisols had the highest mean KRF values and Acrisols had the lowest. The studied 42 soil samples showed variations of KRF values for ammonium acetate ranged from 1.08 to 3.85, and a median of 2.00 (Figure 4.1). Less than 30% of the samples had KRF values between 1.22 and 1.5 and at most 70% had KRF values between 1.50 to 2.00 for Mehlich-3, while more than 25% of samples had KRF values between 2.5 to 3.85 for Ammonium acetate, whilst 50% had ≤2.5 and that 24% had ≥3.85, with Bray No.2 having at most 30% of KRF values between 0.76-0.90 (Figure 4.2). There was a significant difference between the three studied extractants (Table 4.3) at $P < 0.05$. Strong correlations were observed between the extractants used Mehlich-3, Ammonium acetate and Bray No.2 (Table 4.3). The correlation coefficients (r) of Ammonium acetate with Bray No.2 and Mehlich-3 were 0.85 and 0.81, respectively from KRF values. The relationship between all the extraction tests studied showed a poor correlation between the potassium buffering capacity for the ten selected soil samples (Table 4.3).

Table 2.2: Mean of soil potassium requirement factors for the three evaluated soil extractants. Values in parentheses represent their range. Soil groups (ranges) not presented as marked with (-) were undeterminable due to their number of samples.

	Potassium requirement factor (kg K ha^{-1} per unit soil test value)		
Soil type	**Mehlich-3**	**Ammonium acetate**	**Bray No.2**
Acrisols	1.00	1.39	0.48
	-	-	-
Ferralsols	1.35	1.99	0.66
	(1.03-1.87)	(1.08-2.91)	(0.51-0.80)
Fluvisols	1.29	2.59	0.72
	(0.81-1.80)	(2.1-3.11)	(0.66-0.78)
Leptosols	1.17	1.71	0.74
	(1.01-1.34)	(1.14-2.37)	(0.56-0.89)
Luvisols	1.42	2.2	0.72
	(1.08-1.87)	(1.31-3.31)	(0.56-0.85)
Nitisols	1.09	2.25	0.69
	(1.00-1.19)	(1.91-2.58)	(0.64-0.75)
Plinthosols	1.3	2.38	0.67
	(1.13-1.98)	(1.56-3.85)	(0.49-0.86)
Vertisols	1.38	2.52	0.70
	-	-	-

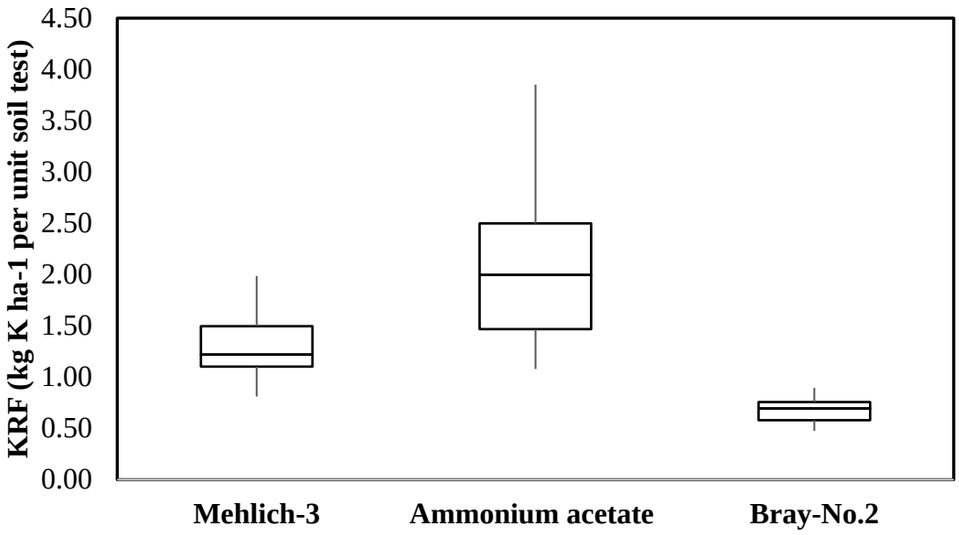

Figure 4.1: Variations in potassium requirement factor of all soils studied for three extractants as indicated by boxplots. The two vertical lines which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in extractants. The middle horizontal line in the box represents the median (50th percentile).

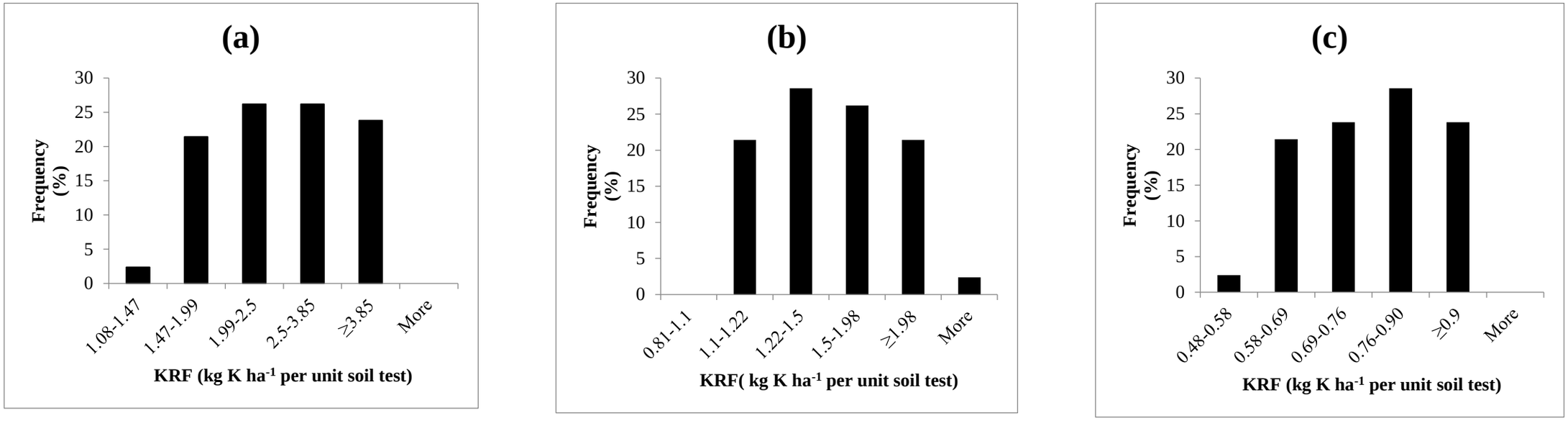

Figure 4.2: Frequency distributions of potassium requirement factor using the (a) Ammonium acetate (b) Mehlich-3 (c) and Bray No.2.

Table 4.3: Linear correlation coefficients (r^2) describing relationships between the three extractants studied

	Parameters		
Parameters	**KRF Mehlich-3**	**KRF Ammonium acetate**	**KRF Bray No.2**
KRF Mehlich-3	-		
KRF Ammonium acetate	0.81*	-	
KRF Bray No.2	0.82*	0.85*	-
#PBC	0.31*	-0.27*	0.12*

* Significant at $P < 0.05$

#**PBC**: potassium buffering capacity (***n = 10***)

4.3. Relationship between potassium requirement factors with soil properties

The correlation between KRF values and soil physicochemical parameters are shown in (Table 4.4). This was done to test if the mentioned parameters behave the same throughout the different soil systems. Exchangeable K was positively correlated with the KRF values for the ammonium acetate extraction test (r = 0.45), while sand, sample density and exchangeable acidity were inversely correlated with all other extraction tests studied (Table 4.4). Contrary, the KRF (Mehlich-3, NH_4OAc and Bray No.2) values for all extractants poorly correlated with clay % with r = 0.05, 0.07 and 0.13, respectively. Total carbon, cations, and pH (KCl) also correlated relatively poorly with all the evaluated extractants (Table 4.4).

Table 4.4: Linear correlation coefficients (r^2) describing relationships between the three extractants studied with the physicochemical properties (***n = 42***)

Extraction test	Particle size distribution			Sample density	Exchangeable bases			Exch. Acidity	Total cations	Total carbon	pH (KCl)
	Clay	Silt	Sand		K	Ca	Mg				
$KRF_{Mehlich-3}$	0.05*	0.09*	-0.09*	-0.16*	0.17*	0.26*	0.15*	-0.23*	0.23*	0.33*	0.35*
$KRF_{ammonium\ acetate}$	0.07*	0.05*	-0.03*	0.16*	0.45*	0.38*	0.27*	-0.34*	0.36*	0.10*	0.29*
$KRF_{BrayNo.2}$	0.13*	0.29*	-0.34*	-0.01*	0.01*	0.22*	0.23*	-0.29*	0.21*	0.13*	0.09*

Correlations are significant at *$P < 0.05$

4.4. Potassium Q/I parameters

The determination of potassium Q/I parameters were selected based on differences in soil groups ten different soil samples to account for differences in soil forms**.** The values of equilibrium activity ratio of potassium (AR^K) ranged between 0.00070 and 0.00275 $(mol/L)^{0.5}$, with Soil no.31(Plinthosol) showing the lowest AR^K values and Soil no.14 (Plinthosol) having incomparably the highest value, amongst the ten selected soils (Table 4.5). Labile K values (-ΔK) varied from 0.234 to 0.0471 (cmol/kg) with Soil no.31 having lowest while Soil no.14 had the highest labile K values. The potassium buffering capacity (PBC^K) of the soils averaged 76.3 and ranged from 62.7 to 95.1 cmol/kg/ $(mol/L)^{0.5}$ with the highest PBC^K values were recorded for Soil no.41 (Luvisols) with lowest for Soil no.42 (Leptosols). There were poor correlations between the studied Quantity-Intensity (Q/I) parameters and physicochemical properties observed (Table 4.5). Silt showed good correlations with AR^K (r = 0.65) and -ΔK (r = 0.71). Exchangeable K showed negative correlations with AR^K (r = -0.11), -ΔK (-0.12) and PBC^K, (-0.15). The correlation between -ΔK and AR^K had the strongest correlation r = 0.91 (Table 4.6). As expected, there were poor correlations between clay% and pH (KCl) amongst all the Q/I parameters studied.

Table 4.5: Potassium Q/I parameters of selected soil samples (***n = 10***)

Sample Name	AR^K $(mol\ l^{-1})^{0.5}$	$-\Delta K$ $(cmol\ kg^{-1})$	PBC^K $[(cmol\ kg^{-1}/ (mol\ l^{-1})^{0.5}]$
S1(Ferralsols)	0.00222	0.142	63.79
S4 (Ferralsols)	0.00156	0.144	91.94
S6 (Ferralsols)	0.00152	0.101	66.33
S14 (Plinthosols)	0.00275	0.234	85.04
S22 (Fluvisols)	0.00094	0.073	77.77
S26 (Nitisols)	0.00139	0.088	63.48
S31 (Plinthosols)	0.00070	0.047	66.94
S33 (Luvisols)	0.00078	0.071	90.03
S41(Luvisols)	0.00139	0.132	95.01
S42 (Leptosols)	0.00244	0.153	62.69
Mean	0.00157	0.118	76.30
Min	0.00070	0.234	62.69
Max	0.00275	0.0471	95.01

Table 4.6: Linear correlation coefficients (r^2) describing relationships of potassium Q/I parameters with selected soil physicochemical properties for the studied soils (***n = 10***).

Soil characteristics	AR^K	$-\Delta K$	PBC^K
Exchangeable K	-0.11*	-0.12*	-0.15*
pH (KCl)	-0.06*	0.0008*	0.14*
Total cations	0.12*	0.04**	-0.23**
Total carbon	0.05*	0.19*	0.34**
Clay	0.16**	0.06*	-0.34*
Silt	0.65*	0.71**	0.03*
Sand	-0.47*	-0.41*	0.25**
$-\Delta K$	0.91**	-	0.21*
PBC^K	-0.17*	0.21**	-

*Correlations are significant at $P < 0.05$

** Correlations are significant at $P < 0.01$

4.5. Conformation to Schofield ratio law

The concentrations of Ca, Mg and K at equilibrium increased with initial concertation in solution (Table 4.7). However, the proportions of concentrations of Ca and Mg in the initial solutions were varied to the proportions of those in soil solution. The ratio ($aK /(aCa+aMg)^{0.5}$) was approximately equal for all the equilibrium solutions in each selected soil and its variation was from 0.0050 to 0.0183. The study for conformation to Schofield ratio law as governed by activity ratio (Table (4.7) showed that the Law was obeyed hence ion pair K-(Ca+Mg) conformed to Ratio Law.

Table 4.7: The activity ratios of K in the studied soils (***n =10***)

Sample	**mg L^{-1}**			**(Moles/L $)^{1/2}$**	**Sample**	**mg L^{-1}**			**(Moles/L $)^{1/2}$**
	Ca	**Mg**	**K**	**aK/√(aCa+aMg)**		**Ca**	**Mg**	**K**	**aK/√(aCa+aMg)**
S1 (Ferralsols)	3.98	13.9	4.91	0.0050	**S26 (Nitisols)**	2.63	2.08	4.27	0.0091
	16.7	27.1	7.32	0.0051		9.30	5.66	7.39	0.0091
	40.5	43.0	10.2	0.0054		25.8	27.1	13.9	0.0091
S4 (Ferralsols)	4.78	12.8	14.5	0.0152	**S31 (Plinthosols)**	9.36	3.89	3.41	0.0160
	17.0	20.3	20.1	0.0152		18.3	16.9	17.9	0.0146
	29.9	34.6	25.9	0.0152		25.9	27.9	29.1	0.0164
S6 (Ferralsols)	5.43	7.11	6.98	0.0090	**S33 (Luvisols)**	8.95	3.13	9.92	0.0108
	16.5	21.9	11.9	0.0089		18.3	17.2	21.8	0.0136

	38.9	45.9	17.4	0.0090		23.9	33.3	31.7	0.0143
S14 (Plinthosols)	3.84	8.85	7.00	0.0086	**S41 (Luvisols)**	5.26	4.59	2.28	0.0096
	13.4	38.6	14.0	0.0088		10.5	16.3	12.4	0.0093
	38.1	46.9	17.1	0.0088		16.0	32.9	29.5	0.0097
S22 (Fluvisols)	4.38	5.97	13.1	0.0183	**S42 (Leptosols)**	6.39	3.93	4.02	0.0104
	18.9	12.1	21.2	0.0183		11.4	16.6	11.7	0.0102
	32.7	29.6	29.5	0.0180		19.9	37.5	33.5	0.0107

4.6. Charge characteristics

The intersection points of CEC and AEC represented the PZNC and CEC values were greater than those of AEC. The point of zero net charge (PZNC) of all the soils ranged from 1.2 to 5.2. Fluvisols had the lowest PZNC (1.35), while the highest was recorded for Vertisols at 3.1 (Table 4.7). Amongst the 42 soils, the PZNC of 15 soils was not determined, due to the lack of intersection between AEC and CEC (Appendix 4.3). The overall mean of point of zero salt effect of the soils was at 5.39 with it ranging from 4.1 to 7.4. The mean values point of zero salt effect (PZSE) varied amongst the grouped soils with Fluvisols having the highest, followed by Nitisols and Acrisols, whilst Luvisols had the lowest. Amongst the studied soils ten had undetermined PZSE (Table 4.7/Appendix 4.3). The cation exchange capacity (CEC) and anion exchange capacity (AEC) values where determined at neutral pH in cmol/kg for each soil sample. Vertisols had the highest CEC and AEC mean values, followed by Plinthosols and Ferralsols, while Luvisols had lowest values. The net surface charge (NSC) was determined from differences of CEC and AEC.

Table 4.8: Mean values of Point of zero net charge (PZNC), Point of zero salt effect (PZSE), Cation exchange capacity (CEC), Anion exchange capacity (AEC), Net surface charge (NSC) and pH (H_2O and KCl). Values in parentheses represent ranges. Soil groups (ranges) not presented were undeterminable due to their number of samples.

Soil type	PZNC	PZSE	CEC	AEC	NSC
			cmol/kg		
Acrisols	*n.d*	5.20	56.7	16.9	-39.8
	-	-	-	-	-
Ferralsols	1.54	4.09	58.8	12.5	-46.3
	(1.2-5.2)	(4.1-7.4)	(16.0-114)	(0.72-39.14)	-(96.34 -7.73)
Fluvisols	1.35	5.85	50.65	12.9	-37.7
	-	(5.4-6.3)	(28.59-72.71)	(9.19-16.78)	-(55.93-19.40)
Leptosols	2.88	4.46	36.9	8.3	-28.6
	(1.6-4.8)	(4.5-6.6)	(27.74-56.15)	(0.80-17.73)	-(47.45-16.66)
Luvisols	1.42	2.77	27.5	5.3	-22.1
	(1.5-2.7)	(5.4-6.3)	(28.57-72.71)	(9.19-16.78)	-(55.93-19.40)
Nitisols	2.15	5.55	29.1	5.6	-23.5
	-	(4.6-6.5)	(26.73-31.51)	(4.79-6.40)	-(25.12-21.94)
Plinthosols	1.61	3.79	68.3	11.2	-57.1
	(1.4-3.7)	(4.4-5.9)	(36.64-90.84)	(0.64-40.74)	-(90.20-30.25)
Vertisols	3.10	5.40	84.7	28.1	-56.5
	-	-	-	-	-

n.d., Not Detected

Table 4.9: Linear correlation coefficients (r^2) describing relationships between the point of zero salt effect (PZSE) and point of zero net charge to $\Delta pH_{(KCl-H2O)}$, pH_{KCl}, pH_{H2O}, cation exchange capacity (CEC) and anion exchange capacity (AEC).

	PZSE	PZNC
$\Delta pH_{(KCl-H2O)}$	-0.17*	-0.21*
pH_{KCl}	0.12*	0.07*
pH_{H2O}	-0.03*	-0.14*
CEC	0.38*	-0.14*
AEC	0.08*	-0.19*

Marked with (*) indicate correlations significant at $P < 0.05$

CHAPTER FIVE: DISCUSSION

Soil fertility of K and the other nutrients in agricultural field probably increases with successive and excessive applications of K fertilization. Soil diagnosis has proven to be an essential tool to achieve a target yield and to avoid excessive fertilization (Sunaga et al., 2015). The literature reviewed has shown that apart from soil properties, potassium equilibria has vast effect in implicating the process of precisely estimating fertilizer K requirements.

Particle size distribution and textural class for soils studied ranged from mostly sandy clay loam to clay with clay content ranging from 6% to 30 % (Appendix 1). The observed results could confirm that soil texture has a valuable impact on several properties and processes, which may affect K dynamics. The Vertisols had the highest clay content of up to 30.2% with Ferralsols group having lowest mean clay content at 14.70% (Table 4.1). High clay content observed for Vertisols confirm the description that such soils are heavy on clay content with a high proportion of swelling clays.

Since topsoils were used for this study, the translocation process as a function of rainfall can thus account for clay differences. This argument is perhaps further supported by high exchangeable acidity in Acrisols with low clay percentage. This may also be impacted by leaching of basic cations ($Ca^{2+,}$ Mg^{2+} and K^{+}) under high rainfall areas, therefore leading to an increase in acidity (Al^{3+} and H^{+}) (Rahman et al., 2018). While fine textured soils tend to hold more K than those of coarser texture, this is influenced by the larger particles which causes leaching of K into soil solution (Wakeel et al., 2002). Overall, most of the studied soils had sandy textures, particularly sandy loam, sandy clay loam and loamy sand soils (Appendix 4.1). Such sandy soil range have limited plant nutrient availability, low water holding capacity and a higher permeability. The large particles 'macropores', support free water movement through soil. This, together with lower CEC, results in losses of K from soil through leaching.

In the current study, total organic carbon percentage of soils ranged from very low to medium. The soil organic matter is a major source of plants nutrients and improves physical soil properties i.e. porosity, structural stability and water holding capacity (Seremesic et al., 2011). Most of the soils studied had total OC contents above 2% threshold value and they indicate that soils are not susceptible to aggregate destabilization (Howard and Howard, 1990). The increase in organic matter tends to improve cation exchange capacity and biological diversity in soils. The availability of K in such soils would be limited.

Soil pH plays a vital role in affecting nutrient availability, mobility, and solubility in soils necessary for plant growth. The pH of the studied soils is illustrated in (Table 4.1) and it ranged from acidic (3.78) to near neutral (6.47). According to Goulding, (2016) pH values between 5.5-6.8 are ideal for the availability of nutrients for most crops (FSSA, 2003). Luvisols had the highest mean pH (KCl) values with the Acrisols having the least (Table 4.1). The low pH values observed in the soil samples would have a vast impact into reducing the availability of potassium. Therefore, because of acidity in the soils , cation exchange sites that hold essential cations such as $Ca^{2+,}$ Mg^{2+} and K^{+} in the soil would be negatively charged. Consequently, these cations are leached resulting in the depletion of base cations from the soil. The losses of these nutrient cations from soil solution or soil exchange sites result in nutrient imbalance in the soil (Rahman et al., 2018). The results for amounts of exchangeable K and those of surface charge characteristics in the studied soils supported such an argument, which are in an optimum range to influencing K availability.

Soil surface charge characteristics (PZNC and PZSE) as pH-dependent has an effect to K availability based on K^{+} ions transportation in the soil system. The studied PZNC values for the soils and it effect to K availability was based on CEC and AEC. Moghimi et al. (2013) reported that, in conditions where protons are exchanged for electrolyte cations soils with a net negatively charged surface, pH is greater than PZNC and the increasing ionic strength of the solutions will cause increased negative surface charge and lowered PZNC. In the experiment the graphs clearly displayed that PZSE was on the acid side or below the point where equal amounts of acid and base were added. Moreover, such curves in the study concurred with those find by Karak et al. (2005) in their experiment, which opposed the usual trend of higher electrolyte concentration resulting in higher pH below the PZSE. Such that at lower pH values, protons were primarily consumed in the mineral dissolution reactions present in soils instead of generating surface charge.

As reported in the study the lower soil pH values would have effect towards the permanent and variable charges to the soil in retention of K. Therefore, under such acidic conditions, weathering would resonate to liberate K from micaceous and feldspar minerals, enabling K to enter the soluble and exchangeable pools and will have vast impact to K retention. In variable-charge soils increase in acidity has direct effect upon cation exchange capacity, hinders the ability of the soil in retaining K resulting to K being leached out of soil solution. The decline in basic cations i.e. Ca and Mg is impacted effectively in acidic soils leads to vast deficiency

of these cations for plant growth. While increase in acidic soils results to smaller amounts of Mg to remain in exchangeable forms due to reduction in negative charge and accumulate in solution phase being more prone to leaching. The effect of pH on soil charge characteristics would cause implications on K availability and fertilizer K in such soils would be required at limited amounts. This would also be influenced by the effect of cation availability as limited by acidity in soils causing huge impact on K being leached out. Soil tests for plant available K are also used to investigate the K status of soils inorder to estimate fertiliser K requirements

Potassium requirements differences are mainly attributed to the need to overcome the effects of K fixation and release in soil system, mainly determined by clay mineralogy. However, soils with the same extractable K levels do not necessarily have similar K requirements (Barbagelata, 2006). In the study values of KRF expressed as kg K ha^{-1} per mg K L^{-1} ranged from 0.81-1.98; 1.08-3.85 and 0.48-0.90 for Mehlich-3, Ammonium acetate and Bray No.2, respectively. This variations in KRF values on the studied extractants showed that a choice of extractant will have an impact to amounts of K required due to the variability in KRF. However, using a classification by Elephant et al. (2019) where they grouped KRF values into Low (1.5-2.5), Medium (2.5-3.5), High (3.5-4.5) and Very high ($\geq$ 4.5) in their study on Ambic would help motivate for ranges on KRF determined by ammounium acetate in current study. Moreover, based on literature Ambic extraction method works in a similar routine as ammonium acetate and these ranges can reasonably be used for KRF based on ammonium acetate for the current study. Therefore, it is interesting to note that from the results, KRF values determined by ammonium acetate were in medium range compared to Mehlich-3 and Bray No.2 which resulted to low ranges. However, medium KRF values would imply less strongly buffered the soil and would require less fertilizer inorder to change soil test value.

The variations of KRF values between soil groups could be impacted by clay content and differences in land use. Soil types such as Ferralsols and Plintosols as in case of the study are usually associated with large quantities of highly weathered minerals such as kaolinite and sesquioxides and as a result cause high KRF values. The high presence of kaolinites in this soil groups would imply that there would be high K retention as such most of the K applied will move into soil solution leading to higher KRF. While those such as Acrisols, Leptosols, Luvisols and Nitisols are often formed from various parent materials which include but not limited to alluvium material (IUSS working group WRB, 2014). Hence such findings in the study have also confirmed the extensive literature that variations in KRF values could be influenced by varying clay content in the soil system, which then had a huge impact with

resulting to lower KRF values in such groups. These then confirm that when making potassium fertilizer recommendation would require less fertilizer application possibly due to high K-fixation in this soil groups (Acrisols, Leptosols, Luvisols and Nitisols). Such findings would conclude that at different soil groups supports for the differences in KRF values.

The variations of KRF estimated through using ammonium acetate showed more than 50% of samples had KRF values ≤2.5 while approximately 24% had ≥3.85. This distributions amongst ammonium acetate recorded signified for the majority of soils studied, K fertiliser recommended will be over applied, while for 24% the K fertiliser will be under-applied in such soils. These conclusions were based on studies done by Elephant and Miles (2016) involving South African sugarcane soils using Ambic as a specific method, reported that the use of KRF 3.0 threshold, instead of determined values between 1.5 and 2.5, would result in over application of fertilizer K. While (Brady and Weil, 2007) reported, that soils with KRF values below 2.0 significantly indicate potassium release impacted by wetting and drying, while KRF values between 2.0 and 2.5 represent soils with limited K fixation and retention.

Amongst the evaluated extractants comparable relationships was observed between Mehlich-3 and Ammonium acetate with strong positive correlations occurring between these two methods. These findings agreed with previous studies done on comparing Mehlich-3 and NH_4OAc which showed a significantly strong correlation between these two extractants (Thompson, 1995 ; Grewal et al., 2017). Numerous studies seemed to be finding almost similar results, (Mehlich, 1984) have shown that Mehlich-3 extractant gives values for K that are similar but slightly lower than neutral 1M NH_4OAc with a correlation coefficient ($r = 0.98$). These findings were also similar to those of Hanlon and Johnson (1984), who reported that neutral 1M NH_4OAc method resulted in much higher amounts of K than Mehlich-3 although these were highly correlation ($r = 0.99$). Schmisek et al. (1998) also reported a correlation coefficient (r) of 0.97) when comparing the use of Mehlich-3 and 1M NH_4OAc. In the current study the comparison among the three extractant, showed good correlation., The relationship between Mehlich-3 and NH_4OAc was 0.81. It can then be concluded that in the present study, the best suited test method is Ammonium acetate and Mehlich-3. Therefore, this demonstrates that ammonium acetate and Mehlich-3 methods extract comparable amounts of K across different soils, with high correlation between both. The Bray No.2 method extracted larger amounts of soil K, most probably from the non-exchangeable K pool and extracted different amounts of K from soils different in texture and clay mineralogy. Based on these results it can be concluded that Mehlich-3 and Ammonium acetate extractant could be adopted to determine

the K available in soils of KwaZulu Natal to guide the recommendations of K fertilizers. Additional field research, however, is needed to improve Bray No.2 predictions.

The linear correlation coefficients between KRF and soil physicochemical parameters were evaluated also as shown in Table 4.6. This was done to test if the mentioned parameters can be used as substitute parameters that can be later used to predict KRF. Exchangeable K was positively correlated with the KRF values when the ammonium acetate extractant was used (r = 0.45). Such positive correlation could be expected since exchangeable K is not only influenced by soil properties but also by K inputs and K removals in soil system (Khan et al. 2014). Therefore, this parameter could show implications on K availability and when making fertilizer recommendations, hence its likely to impact to K fixation capacity which is likely to affect plant-availability of added K. The KRF (Mehlich-3, NH_4OAc and Bray No.2) values for all extractants poorly correlated with clay % with r = 0.05. These results concur with the findings by Johnston (1999) who found no correlation between KRF measured in Ambic and % clay. This could represent obstacles in incorporating KRF and soil physicochemical properties for making fertilizer recommendations, given that there is no routinely measured parameter that correlates with KRF. Quantity-intensity (Q/I) relationships also provides an alternative to soil K testing for better understanding of K dynamics and more informed fertilizer recommendations.

Potassium Q/I relations play massive role in predicting K^+ availability to plants and to understanding and evaluating K^+ fertility status of soils (Wang and Scott 2001). In the studied soils PBC^K values ranged from 62.69 to 95.05 cmol/kg/ $(mol/l)^{0.5}$ (Table 4.7), which indicated that medium fertilization K would be required in such soils. However, (Le Roux and Sumner, 1968 ; Zharikova, 2004) concluded that PBC^K values are divided into very low those less than 20 cmol/kg $(mol/l)^{0.5}$ and high those that are greater than 200 cmol/kg $(mol/l)^{0.5}$, assists to making conclusions with regards to how much fertilization this parameter would suggest and thus findings in the studied soils are classified in the moderate range. According to (Le Roux and Sumner, 1968) higher values of PBC imply a constant K^+ availability in the soil over a long period, whilst in soils of low PBC frequent fertilization is recommended. Higher potassium buffering capacity as reported in Soil no.41 (Luvisol) with 95.01 cmol/kg $(mol/l)^{0.5}$, signify that the soil can maintain potassium and resist to potassium level change (Al-Zubaidi et al., 2008). Thus, the moderate PBC^K values of the soils indicates a lesser capacity for maintain K concentration, but they enable a high K intensity. Therefore in-terms

of fertilizer recommendation such parameters would result to medium K recommendation with an indication of better K availability.

The equilibrium activity ratio (ARe^K) is said to be the measure of the availability or intensity of labile K in the soil and represents the K that is immediately available to crop roots (Yawson 2011). The values of AR_e^K amongst the soils studied ranged between 0.00070 and 0.00275 $(mol/l)^{0.5}$ (Table 4.6). Usually the recommended threshold for a non-limited plant growth for activity ratio is said to be ARe^K of 0.002 moles $^{0.5}$/l (Sharma et al., 2012). As such in the studied soils fewer Ferralsols, Plinthosols and Leptosols groups were in a proportion which can supply enough K which is not limited for plant uptake while Luvisols and Fluvisols indicated lower supply to K for plant uptake. According to Beckett (1964b) lower AR_e^K values indicates reduced amounts of potassium for plant uptake and lower exchangeable K levels. The AR_e^K values <0.001 $(mol/l)^{0.5}$ imply that K^+ is absorbed at high affinity (specific) sites whilst values which are >0.01 $(mol/l)^{0.5}$ K^+ is absorbed on planar sites as reported by (Sparks and Liebhardt, 1981). Soils with lower AR_e^K values have low plant-available K and would limit plant growth. Various soils with lower AR_e^K values are attributed by lower clay content values. However, in the current study, poor correlation between AR_e^K and clay content was observed r = 0.16 further supporting the lower AR_e^K values obtained in the study. Whilst those of greater AR_e^K would be associated with greater amount of plant-available K and high exchangeable K levels. Thus, this signifies there would be low need for fertilizer K application in those soils with higher AR_e^K

Labile K parameter among other parameters that were evaluated in the study, represents the available K that participate in ion exchange at equilibrium between soil solids and solution (Zarrabi and Jalali, 2008; Lalitha and Dhakshinamoorthy, 2015). Higher values of the labile K influence greater K^+ release into soil solution causing a larger pool of labile K being available (Sparks and Liebhardt, 1981). In the study labile K values ($-\Delta K$) varied from 0.234 to 0.0471 (cmol/kg) with selected plinthosols having the highest (Table 4.7). However, lower labile K values as recorded for soil no. 31 (plinthosol) (0.234 cmol/kg) are associated with K^+ depletion over a longer period. The lower values are also influenced by presence of montmorillonite clay mineralogy, low clay content and cation exchange capacity (Lalitha and Dhakshinamoorthy, 2015). According to Samadi (2006) those soils of higher values, in the case of soil no. 14 (plinthosol), would attribute to high CEC values for the sample and amount of loosely bound K^+ ions present on the exchange site. However, labile K increases with increase in K fertilization this implies that soils in the study which had higher KRF values would recommend

for high K addition due to increases in labile K in these soils. Overall, it has been better understood from the current study that Q/I parameters are not only centred in estimating K availability for crop improvement, but also provides with knowledge gaps into making fertilizer recommendations.

Strangely, clay was poorly correlated with most of the Q/I parameters (AR^K, -ΔK and PBC^K) with r values of 0.16, 0.06 and -0.34 respectively. However, the poor correlation recorded for AR^K and clay indicates that increase in clay content of the soils resulted into decrease in AR^K. Silt showed good correlations between AR^K, -ΔK r = 0.65, r = 0.71, respectively. This could possibly in future suggest one can adapt to using silt content in estimating AR^K and -ΔK. Exchangeable K showed negative correlations with AR^K (r = -0.11), -ΔK (r = -0. 12) and PBC^K (r = -0.15) which was contrary to Ldigbor et al. (2009) who showed positive correlations ranging from r = 0.63 to 0.75. Moreover, studies done by (Nongqwenga and Modi, 2017) found positive correlations on influential soil properties with potassium Q/I parameters using soils from different bioresource groups in KwaZulu Natal. The correlation between -ΔK and AR^K had the strongest correlation r = 0.91 (Table 4.8). However, such findings can be explained by the competitive relation existing between the activity of K and activity ratio of Ca^{2+} and Mg^{2+} content (Abaslou and Abtahi, 2008 ; Yeledhalli et al., 2010).These relationships are significant and deserved of exploration to further understand potassium dynamics in soils. Such a comprehension can ease modelling and prediction of K behaviour in soils. The activity ratio of K involving the effect of complementary ions (Ca and Mg) may prove to be a better measure of potassium availability in soils based on conformity to Schofield ratio law (Pasricha, 1983).

To account for K intensity and buffer capacity the exchange between K and other cations need to be accounted for, because capacity and intensity do not only depend on K levels. However, (Woodruff, 1955) reported that K-Ca interactions can explain K availability, modifications have been applied to Woodruff's theory to incorporate Mg, thus K availability can be explained by the activity of (Ca+Mg) as a single unit. The assumption of using Ca and Mg as reference cation is that their activity is dominant in soil exchange system, and it has proved that in acidic soils where activity of Al^{3+} and H^+ is significant the K-Ca+Mg binary system is not sufficient enough in explaining K dynamics in soil system (Tinker 1964a; Tinker 1964b). The values of activity ratios normally reflect the chemical potential of the soil. High activity ratio value simply means more potassium available for plant absorption (Schofield and Taylor, 1955). However, accuracy of the method, and for soils which were selected based on distinguished

soil groups, it is clear from Table (4.7) that the ion pair K-(Ca+Mg) conforms to Ratio Law. This conformation was based on that at equilibrium the activity ratios ($aK /(aCa+aMg)^{0.5}$) were constant, unaffected by the concentration of the solution and soil solution ratio (Nafady, 1972). The ability of a soil to supplying nutrient ions is governed by ion exchange reactions which also plays a vital role in plant nutrition. The activity ratio of K involving the effect of complementary ions (Ca and Mg) may prove to be a better measure of potassium availability in soils (Pasricha, 1983).

The findings of the study conformed to ratio law. This was supported by the activity ratios values of each given soil having same or approximately equal for all solutions regardless of their concentrations and proportions of Ca to Mg. Findings of the current study concurred with previous studies done to evaluate conformity of Ratio laws. Taylor (1958), when evaluating ion pair K-(Ca+Mg), reported that two out of four soils did not conform to the law while those that strictly obeyed the law did so on low potassium status. Conversely, on their study based on K-Ca exchange isotherm for kaolinite Beckett and Nafady (1967) concluded that at low pH exchangeable ions, which are associated with edge sites with excess negative charge obeyed the ratio law, while those associated with planar surfaces with positive charges did not obey the law. Le Roux (1966) investigated a variety of Natal soils and found that the ion pair of K-(Ca+Mg) fully conforms to the Ratio law. The study proved that the conformity of various soils to ratio law would direct a huge impact to making further fertilizer recommendations hence complement of labile K and Ca possessed same activity ratio proving the law being obeyed. Therefore, the study managed to complement confirmation to ratio law with regards to K availability inorder to make fertilizer K recommendations.

CHAPTER SIX: GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

6.1. General discussion

Soil tests for plant available K are used worldwide to determine the K status of soils inorder to estimate fertiliser K requirements for specific yield goals. Currently, adapting to soil testing methods for K would not only maximize crop productivity and quality, but also avoid long term K depletion of fertile agricultural lands. The main objective of the study was to study K equilibria and its relation to surface charge characteristics and compare potassium requirement factor (KRF) derived from various extractants and its effectiveness to making fertilizer recommendations. This involved investigating effectiveness of surface charge characteristic and potassium Q/I relation in making fertilizer recommendations on KwaZulu Natal soils (Midlands). Previous studies have shown the importance of using different extractants to be estimating potassium would provide feasible information to making fertilizer recommendations, but their inclusion in KRF with charge characteristics and potassium Q/I relations remains relatively unexplored.

Fertilizer K requirements resulting from the use of soil testing K methods (extractants) had vast effect in making conclusions for the best suitable method to making fertilizer recommendations. In the study, variations in KRF values on the used extractants showed that a choice of extractant will have an impact to fertilizer recommendations due to the variability in KRF. In the study KRF values were higher for ammonium acetate, with Mehlich-3 having medium and Bray No.2 had lowest KRF values. These findings are coupled with the fact that when making fertilizer recommendation, $KRF_{\text{Ammonium acetate}}$ will suggest that a soil will require more fertilizer to change a soil test, $KRF_{\text{Mehlich-3}}$ a soil will require optimum amounts of fertilizer K in changing the soil test whereas for $KRF_{\text{Bray No.2}}$ lower amounts of fertilizer K would be required to change soil test unit. Furthermore, there was a strong positive correlation between the two studied extractants, Mehlich-3 and Ammonium acetate. These findings agreed with previous studies done on comparing Mehlich-3 and NH_4OAc which showed a significantly strong correlation between these two extractants (Thompson, 1995; Grewal et al., 2017). The linear correlation coefficients between KRF and soil physicochemical parameters were evaluated and showed poor correlation. This could represent obstacles, for future studies in incorporating KRF and soil physicochemical properties for making fertilizer recommendations, given that there is no routinely measured parameter that correlated with KRF.

The findings of the study suggested that charge characteristics as influenced by soil pH has an effect to K availability based on K^+ ions transportation in the soil system, soils were of low pH and this consequence resulted to K depletion and nutrient imbalance in the studied soils. Therefore, effect of soil pH on soil charge characteristics had an influence on the response of soils to K fertilization. This also caused effect on cation availability as limited by acidity in soils causing huge impact on K being leached out and when making fertilizer recommendation K would be over-estimated as a results of K depletion in acidic soils. Quantity-intensity (Q/I) relationships also provides an alternative to soil K testing for better understanding of K dynamics and more informed fertilizer recommendations. In the study Q/I parameters were investigated for insightful background in how they affect K availability and to making fertilizer recommendations. In the studied parameters, potassium buffering capacity was found to be moderate and this indicated a lesser capacity to maintaining K concentration levels in the soil. Therefore in-terms of fertilizer recommendation this Q/I parameter resulted to medium K fertilizer to change the soil unit with an indication of better K availability. The equilibrium activity ratio values were mostly high, and this signified that there would be low need for fertilizer K application in those soils with higher AR_e^K. The study proved that the conformity of various soils to ratio law would direct a huge impact to making further fertilizer recommendations hence complement of labile K and Ca possessed same activity ratio proving the law being obeyed. Therefore, the study managed to complement confirmation to ratio law with regards to K availability inorder to make fertilizer K recommendations.

6.2. Conclusions

Soil tests for plant available K are also used to investigate the K status of soils inorder to estimate fertiliser K requirements. Potassium requirements differences are mainly attributed to the need to overcome the effects of K fixation and release in soil system, mainly determined by clay mineralogy. In the study, Ammonium acetate and Mehlich-3 were both able to extract almost similar amounts of potassium, which were slightly lower than those determined by Bray no.2 extractant. The variations of potassium requirement factor (KRF) values across the variety of soils with using the standard method ammonium acetate signified that for the majority of soils studied, K fertiliser recommended will be over applied, while for a minority the K fertiliser will be under-applied in such soils of KwaZulu Natal. The KRF levels amongst the studied extractants (Mehlich-3 and Bray No.2) were different relative to the ammonium acetate as a standard method as such different were expected as each extractant makes use of different chelating agents. The comparability of KRF values extracted by Mehlich-3 and ammonium

acetate reported positively good correlation. The findings of the study recommend the use of Mehlich-3 and Ammonium acetate as the most convenient methods of measuring exchangeable K and KRF hence these two methods have an ability to extracting other elements that are important in soil testing rather than the use of Bray No.2. The study showed that KRF for the extractants was poorly correlated with the most fertilizer influencing parameter (Potassium buffering capacity) and clay and carbon contents. In this study, some soils had a high K intensity and lower in PBC^{K}, indicating that these soils will require frequent K fertilization. The topsoils samples showed a variation between PZSE and PZNC. Moreover, this surface characteristics factors were poorly correlated with pH affecting parameters. The study proved that the conformity of various soils to ratio law would direct a huge impact to making further fertilizer recommendations hence complement of labile K and Ca possessed same activity ratio proving the law being obeyed. Therefore, the study managed to complement confirmation to ratio law with regards to K availability inorder to make fertilizer K recommendations.

6.3. Recommendations for future studies

Its recommended that further studies could possibly establish the applicability of using routinely measured silt to estimate the Q/I parameters and deciding whether fertilizer K would be required.

CHAPTER SEVEN: REFERENCES

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APPENDIX:

APPENDIX 1: Physical and chemical properties of soils (***n* = 42**)

Sample ID	Particle-size distribution (%)			Texture Class	Sample Density (g ml^{-1})	Total Organic Carbon (%)	pH (KCl)	Exchangeable bases (mg L^{-1})			Exch.acidity (cmol L^{-1})	Total cations (cmo L^{-1})
	Clay	Silt	Sand					K	Ca	Mg		
S1	18	30	22	Silt Loam	1	4.51	4.46	82	1328	622	0.15	12.11
S2	23	11	61	Sandy Clay Loam	0.84	7.87	4.07	188	739	153	1.00	06.43
S3	17	24	47	sandy loam	0.94	6.01	4.47	521	880	193	0.46	07.77
S4	7	19	56	Sandy Loam	0.88	5.74	4.00	197	170	63	2.19	04.05
S5	15	15	44	Clay	1.02	4.34	4.52	138	866	288	0.21	07.25
S6	28	22	27	Sandy Clay Loam	1.05	3.59	4.28	330	922	289	0.54	08.36
S7	9	40	41	Silt Loam	089	5.3	4.12	58	202	68	1.84	03.56
S8	6	20	67	Sandy Loam	1.11	4.05	4.19	56	225	57	1.20	02.94
S9	15	14	56	Sandy Loam	1.19	3.01	4.07	66	521	192	1.12	05.47
S10	10	24	54	Sandy Clay Loam	1.04	4.37	4.17	118	346	135	1.42	04.56
S11	24	39	17	Clay	11.5	3.1	4.85	131	1265	485	0.20	10.84
S12	19	28	36	Clay	1.15	2.27	4.91	223	1053	281	0.15	08.29
S13	19	40	19	Loam	1.05	3.45	4.63	79	1357	497	0.31	11.37
S14	25	40	16	Clay	1.12	3.23	4.83	90	1452	528	0.09	11.91
S15	30	34	16	Clay Loam	1.1	4.33	4.59	117	1966	968	0.15	18.23
S16	21	24	32	Sandy Clay Loam	1.04	3.68	5.36	104	1756	384	0.21	12.40
S17	27	22	29	Sandy Clay Loam	0.97	2.36	4.25	227	769	375	0.43	07.92
S18	12	23	53	Sandy Loam	1.03	3.3	4.28	84	461	87	0.62	03.85
S19	12	16	57	Sandy Loam	0.97	2.9	4.17	73	184	51	1.09	02.61
S20	13	11	40	Clay	0.88	4.55	4.61	298	191	79	0.15	02.52
S21	16	13	45	Sandy Loam	0.97	4.91	4.18	47	919	270	0.92	07.85
S22	9	12	69	Sandy Clay loam	1.18	2.39	4.13	99	239	120	1.15	03.85
S23	12	13	63	Sandy loam	1.16	2.43	4.13	29	171	75	1.30	02.84
S24	19	31	32	Clay	1.09	2.34	4.93	116	1111	572	0.07	10.62
S25	14	20	48	Sandy loam	1.09	2.82	5.19	298	958	391	0.07	08.83
S26	28	18	17	Sandy clay loam	1.04	6.78	5.30	175	2926	769	0.12	21.50
S27	18	19	37	Clay	0.96	2.85	4.54	165	718	209	0.26	05.98
S28	20	41	30	Loam	0.93	3.34	4.11	77	479	137	1.20	04.91
S29	19	28	27	Clay	0.88	4.21	4.39	154	1108	239	0.30	08.19
S30	7	16	64	Sandy clay loam	1.13	2.73	4.84	578	702	255	0.12	07.20
S31	20	8	69	Sandy clay loam	1.86	0.66	4.25	78	310	72	0.15	02.49

S32	27	14	57	Sandy clay	0.98	5.62	6.47	95	3008	664	0.04	20.76
S33	21	8	60	Sandy clay loam	1.21	1.84	5.11	65	1420	693	0.14	13.10
S34	19	24	49	Sandy clay loam	1.09	2.87	3.94	127	515	374	0.93	06.90
S35	15	16	59	Sandy loam	0.91	4.98	4.35	146	412	320	0.70	05.76
S36	26	18	46	Clay	1.05	1.77	4.23	70	655	217	0.34	05.57
S37	28	7	63	Sandy clay	0.96	2.76	3.78	52	253	80	1.71	03.76
S38	11	16	50	Sandy loam	1.14	0.79	4.05	49	545	266	0.44	05.47
S39	6	15	70	Loamy sandy	1.16	1.61	6.37	117	1205	513	0.07	10.60
S40	11	21	63	Sandy loam	1.14	2.56	5.62	108	1724	966	0.06	16.89
S41	21	13	62	Sandy clay loam	1.51	7.82	4.75	63	314	90	0.06	02.53
S42	18	6	73	Sandy clay loam	1.14	0.5	4.13	26	172	82	1.41	03.01

APPENDIX 2: Soil potassium requirement factors (KRF) of three evaluated soil extractants for all studied soils ***(n* = 42**)

	Potassium requirement factor (Kg K ha-1 per unit soil test value)		
Sample Number	**Mehlich-3**	**Ammonium Acetate**	**Bray No.2**
S1	1.2	2.3	0.8
S2	1.4	2.2	0.7
S3	1.6	2.8	0.7
S4	1.1	2.3	0.6
S5	1.8	1.8	0.7
S6	1.3	2.5	0.5
S7	1.9	1.9	0.7
S8	1.1	1.4	0.6
S9	1.0	1.4	0.5
S10	1.1	1.3	0.9
S11	1.2	1.5	0.8
S12	1.1	2.4	0.7
S13	1.3	2.2	0.7
S14	1.1	2.5	0.8
S15	1.4	2.5	0.7
S16	1.8	3.1	0.8
S17	1.3	1.9	0.9
S18	1.1	2.7	0.8
S19	1.1	1.3	0.6
S20	1.5	1.4	0.8
S21	1.3	1.7	07
S22	0.8	2.1	0.7
S23	1.7	1.4	0.5
S24	1.2	1.1	0.7

S25	2.0	2.1	0.9
S26	1.0	1.9	0.8
S27	1.2	1.8	0.5
S28	1.1	1.1	0.6
S29	1.7	2.9	0.8
S30	1.2	3.9	0.5
S31	1.2	2.6	0.7
S32	1.9	3.3	0.6
S33	1.2	1.5	0.8
S34	1.1	2.1	0.8
S35	1.2	2.6	0.6
S36	1.2	1.9	0.6
S37	1.1	1.6	0.5
S38	1.0	2.3	0.7
S39	1.1	1.4	0.6
S40	1.7	3.2	0.6
S41	1.5	1.7	0.7
S42	1.0	1.7	0.6

APPENDIX 3: Values of soil extractable K as determined by three different extraction tests (Mehlich-3, Ammonium acetate and Bray No.2), at four concentration levels (0, 30, 90 and 120 mg K kg^{-1}).

Sample Number	**Mehlich-3**	**NH_4OAc**	**Bray No.2**
		mg l^{-1}	
S1	19	27	53
	56	47	116
	90	82	180

	173	104	286
S2	51	25	96
	89	44	170
	108	67	257
	183	105	356
S3	47	23	63
	86	44	133
	118	63	245
	160	88	314
S4	111	34	100
	162	62	229
	199	80	296
	274	115	422
S5	28	21	98
	32	46	185
	62	78	312
	124	121	355
S6	66	37	72
	86	66	162
	127	90	313
	198	112	396
S7	23	27	38
	34	62	126
	73	93	219
	114	125	286
S8	46	21	39
	89	42	145

	157	76	189
	207	149	327
S9	21	20	53
	75	57	116
	115	86	303
	204	151	413
S10	29	28	65
	98	52	115
	150	108	197
	201	160	273

Sample Number	**Mehlich-3**	**NH_4OAc**	**Bray No.2**
		mg l^{-1}	
S11	36	29	48
	92	56	144
	139	112	181
	190	149	289
S12	44	26	51
	52	53	112
	91	76	192
	204	103	291
S13	11	12	42
	41	44	150
	67	63	206
	150	97	298

S14	64	19	139
	107	57	203
	156	69	278
	221	96	363
S15	14	14	41
	38	43	149
	62	63	240
	143	88	305
S16	19	19	44
	54	45	137
	72	57	225
	123	79	278
S17	41	26	26
	77	50	123
	116	76	196
	176	121	235
S18	52	28	48
	93	51	139
	136	74	181
	223	96	296
S19	13	19	49
	61	58	161
	76	118	251
	175	154	379
S20	74	21	59
	105	49	159
	138	85	241

	195	148	301

Sample Number	Mehlich-3	NH_4OAc	Bray No.2
		mg l^{-1}	
S21	9	11	28
	51	53	155
	85	88	248
	146	119	305
S22	25	22	57
	105	61	189
	159	89	261
	224	112	343
S23	15	27	69
	58	52	183
	77	99	326
	126	155	413
S24	32	25	49
	92	39	166
	122	103	218
	186	175	308
S25	48	35	108
	72	54	242
	87	82	287
	140	118	337
S26	86	25	71
	128	55	173

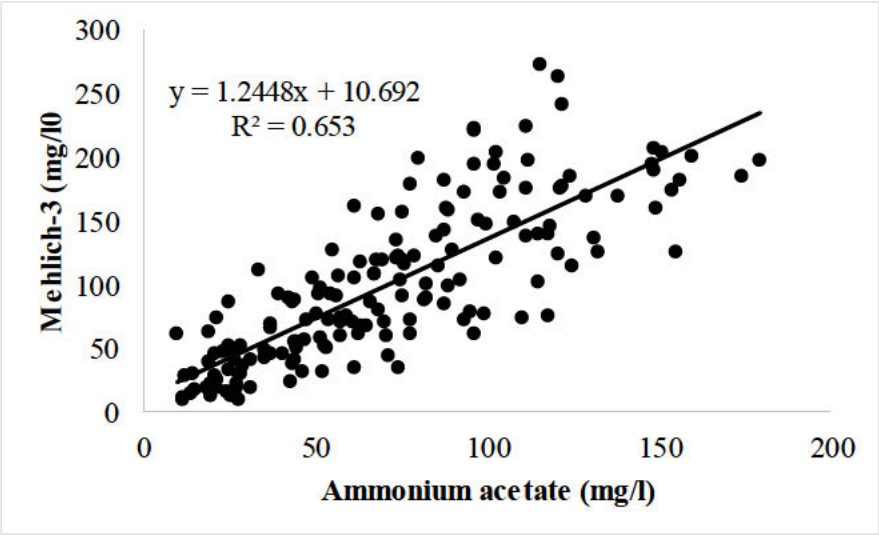
	180	78	260
	264	121	316
S27	30	14	87
	46	40	152
	73	78	339
	176	112	423
S28	28	12	55
	80	69	195
	137	132	303
	199	180	378
S29	43	35	95
	68	65	170
	101	83	247
	147	100	322
S30	35	74	28
	78	95	161
	140	115	294
	178	122	393
S31	39	19	42
	69	37	134
	120	70	214
	183	88	318

Sample Number	**Mehlich-3**	**NH_4OAc**	**Bray No.2**
		mg l^{-1}	
S32	25	22	61

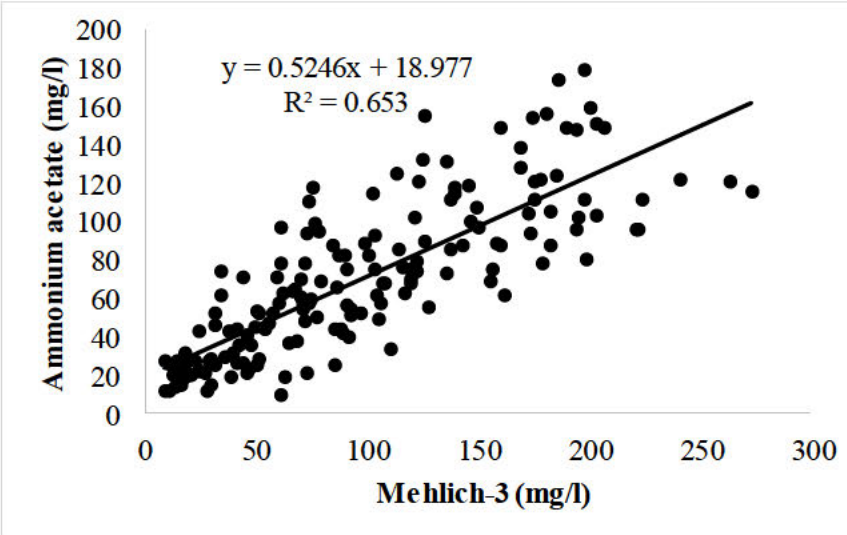
	46	37	126
	75	59	280
	120	75	338
S33	15	24	27
	44	71	174
	74	111	227
	161	149	275
S34	24	43	81
	71	61	193
	104	92	243
	186	125	332
S35	40	31	104
	93	54	179
	122	74	260
	195	102	385
S36	19	31	37
	71	70	196
	99	89	264
	170	129	344
S37	12	25	27
	50	45	200
	104	75	314
	170	139	389
S38	17	15	27
	72	48	152
	108	67	303
	195	96	303

S39	18	21	62
	60	71	172
	103	115	314
	182	156	358
S40	18	19	44
	30	28	167
	54	44	244
	123	74	373
S41	10	27	26
	32	52	169
	62	97	224
	126	133	289
S42	61	10	24
	120	68	172
	174	94	291
	242	122	354

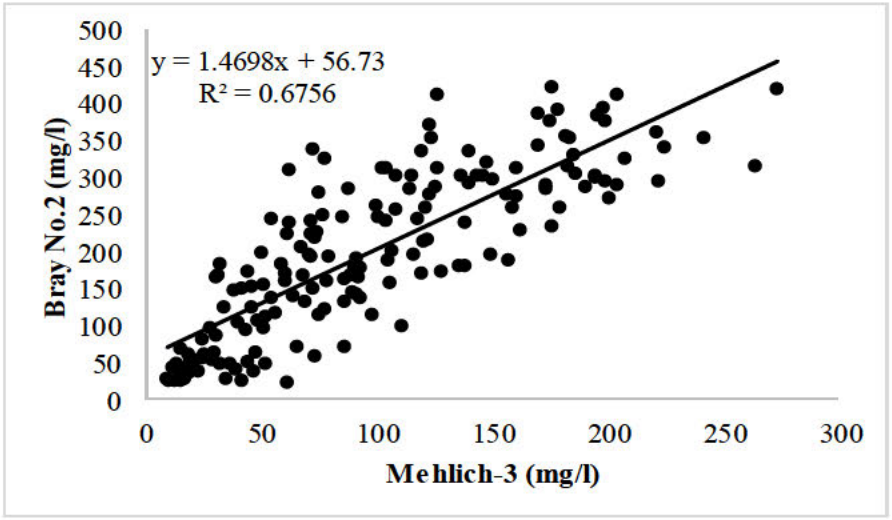
APPENDIX 4: Linear relationship between (a) Ammonium acetate and Mehlich III K, (b) Mehlich III K and Ammonium acetate (c) Mehlich-3 and Bray No.2 (d) Bray No.2 and Mehlich-3 (e) Bray No.2 and Ammonium acetate (f) Ammonium acetate and Bray No.2.



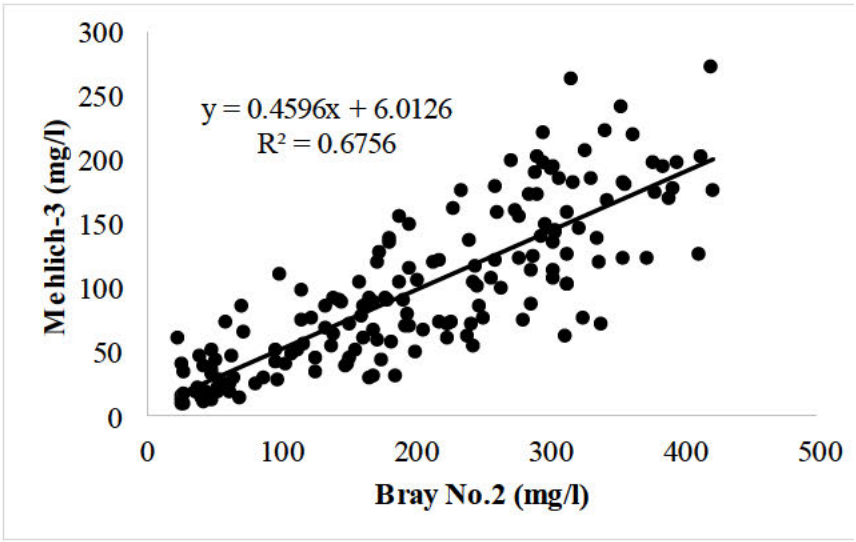
(a)



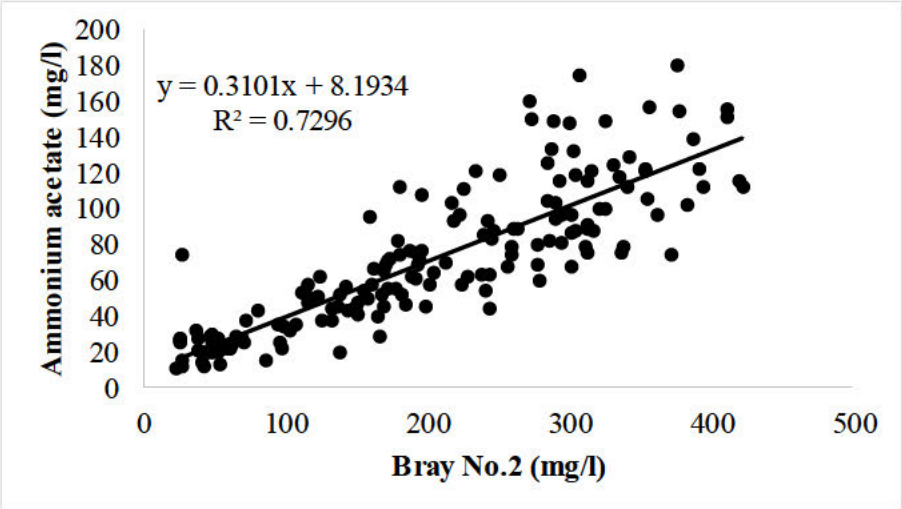
(b)


y = 1.4698x + 56.73
R² = 0.6756
Bray No.2 (mg/l)
Mehlich-3 (mg/l)
0
50
100
150
200
250
300
350
400
450
500

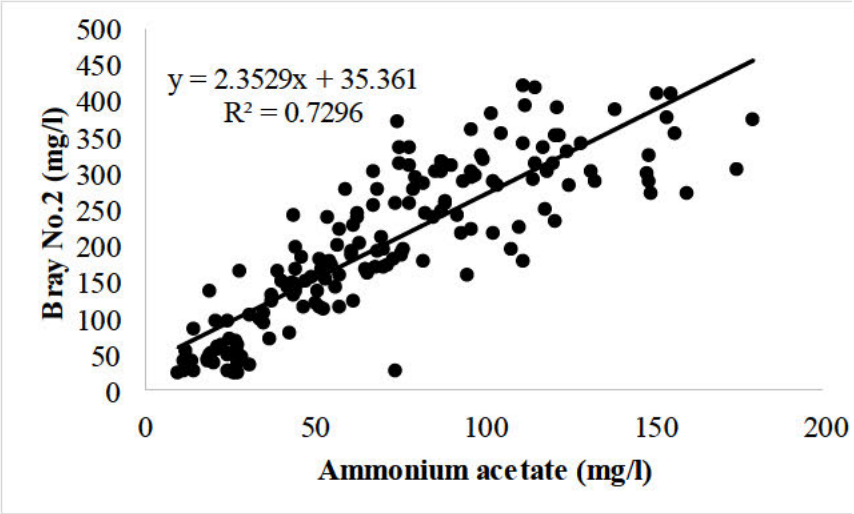
(c)


y = 0.4596x + 6.0126
R² = 0.6756
Mehlich-3 (mg/l)
Bray No.2 (mg/l)
0
50
100
150
200
250
300
400
500

(d)



(e)



(f)

Figure 10: Linear relationship between (a) Ammonium acetate and Mehlich-3, (b) Mehlich-3 and Ammonium acetate, (c) Mehlich-3 and Bray No.2, (d) Bray No.2 and Mehlich-3 (e) Bray No.2 and Ammonium acetate, (f) Ammonium acetate and Bray No.2.

APPENDIX 5: Point of zero net charge (PZNC), Point of zero salt effect (PZSE), Cation exchange capacity (CEC), Anion exchange capacity (AEC), Net surface charge (NSC) and pH (H_2O and KCl).

Sample	PZNC	PZSE	CEC	AEC	NSC	pH	pH
				Cmol/kg		(H_2O)	(KCl)
S1	1.5	4.5	45.04	5.59	-39.44	5.03	4.46

S2	2.1	*n.d.*	31.19	2.40	-28.79	5.22	4.07
S3	4.1	4.1	23.98	7.03	-16.95	5.68	4.47
S4	2.6	4.4	39.06	8.63	-30.43	5.08	4.00
S5	2.2	5.0	48.53	8.95	-39.58	5.96	4.52
S6	*n.d.*	*n.d.*	17.99	8.15	-9.84	5.65	4.28
S7	2.8	*n.d.*	55.81	0.72	-55.09	5.31	4.12
S8	*n.d.*	5	85.24	6.39	-78.85	5.27	4.19
S9	*n.d.*	5.2	56.67	16.86	-39.82	5.74	4.07
S10	3.2	5.5	46.60	11.82	-34.78	5.39	4.17
S11	1.7	5.2	33.53	7.35	-26.19	6.04	4.85
S12	1.6	5.9	27.74	0.80	-26.94	5.88	4.91
S13	*n.d.*	6.1	79.09	39.14	-39.94	5.90	4.63
S14	3.3	5.9	36.64	6.39	-30.25	5.15	4.83
S15	3.1	5.4	84.66	28.12	-56.54	5.38	4.59
S16	2.7	6.3	28.59	9.19	-19.40	5.54	5.36
S17	3.7	5.2	56.15	8.71	-47.45	5.15	4.25
S18	*n.d.*	5.0	36.99	8.95	-28.04	4.85	4.28
S19	1.2	5.1	81.76	5.59	-76.16	4.88	4.17
S20	*n.d.*	5.0	95.73	4.79	-90.93	5.95	4.61
S21	*n.d.*	5.6	114.,00	17.66	-96.34	6.08	4.18
S22	*n.d.*	5.4	72.71	16.78	-55.93	5.39	4.13

S23	2.2	5.1	79.99	27.96	-52.03	5.43	4.13	*n.d.*, Not Detected
S24	2.6	6.0	32.88	7.19	-25.69	5.54	4.93	
S25	*n.d.*	*n.d.*	84.61	40.74	-43.86	6.26	5.19	
S26	4.3	6.5	31.51	6.39	-25.12	5.95	5.30	
S27	5.2	5.7	57.04	8.47	-48.57	5.65	4.54	
S28	*n.d.*	4.8	62.20	39.14	-23.05	5.60	4.11	
S29	1.8	5.3	59.55	8.47	-51.09	5.43	4.39	
S30	*n.d.*	5.7	85.14	17.58	-67.56	5.71	4.84	
S31	1.4	5.3	73.13	7.59	-65.54	5.76	4.25	
S32	2.3	*n.d.*	34.83	13.74	-21.09	6.59	6.47	
S33	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	6.23	5.11	
S34	2.9	*n.d.*	63.18	4.79	-58.39	5.06	3.94	
S35	*n.d.*	4.6	26.73	4.79	-21.94	5.96	4.35	
S36	3.7	5.2	90.84	0.64	-90.20	5.95	4.23	
S37	*n.d.*	4.4	44.56	0.72	-43.84	5.85	3.78	
S38	1.6	*n.d.*	15.96	8.23	-7.73	5.67	4.05	
S39	1.9	7.4	74.78	14.38	-60.40	6.37	6.37	
S40	1.5	6.6	38.31	0.80	-37.51	5.83	5.62	
S41	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	5.41	4.75	
S42	4.8	*n.d.*	34.39	17.73	-16.66	5.68	4.13	